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ELECTRONIC SUPPLEMENTARY INFORMATION

A Novel Catalytic Asymmetric Route towards Skipped Dienes with a Methyl-Substituted Central Stereogenic Carbon

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General Techniques

Starting materials were purchased from Aldrich, Alpha Aesar or Acros and used as received unless stated otherwise. All solvents were reagent grade and, if necessary, dried and distilled prior to use. All reactions were carried out under a nitrogen atmosphere using oven dried glassware and using standard Schlenk techniques. Column chromatography was performed on silica gel (Aldrich 60, 230-400 mesh). TLC was performed on silica gel 60/Kieselguhr F₂₅₄.

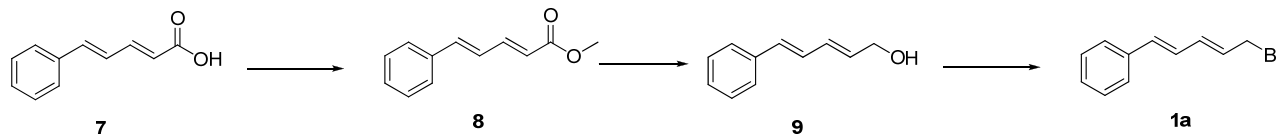
¹H and ¹³C NMR spectra were recorded on a Varian VXR300 (299.97 MHz for ¹H, 75.48 MHz for ¹³C) or a Varian AMX400 (399.93 MHz for ¹H, 100.59 MHz for ¹³C) spectrometer in CDCl₃ unless stated otherwise. Chemical shifts are reported in δ values (ppm) relative to the residual solvent peak (CDCl₃, ¹H = 7.24, ¹³C = 77.0). Carbon assignments are based on ¹³C and APT ¹³C experiments. Splitting patterns are indicated as follows: s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), br (broad).

High resolution mass spectra (HRMS) were recorded on an AEI-MS-902 and FTMS orbitrap (Thermo Fisher Scientific) mass spectrometer. Optical rotations were measured on a *Schmidt+ Haensch* polarimeter (Polartronic MH8) with a 10 cm cell (*c* given in g/100 mL). Enantiomeric excesses were determined by HPLC analysis using a Shimadzu LC-10ADVP HPLC equipped with a Shimadzu SPD-M10AVP diode array detector (Chiralcel OD-H, 250*4.6, 10 μm) or by capillary GC analysis (HP 6890, CP-Chiralsil-Dex-CB column (25 m * 0.25 mm)) using a flame ionization detector.

Racemic products were synthesized by reaction of the allyl bromide and the corresponding organomagnesium reagent at -80 °C in dry dichloromethane in the presence of CuBr•SMe₂ (10 mol%) and PPh₃ (20 mol%).

Synthesis of allylic bromides

Synthesis of ((1*E*,3*E*)-5-bromopenta-1,3-dienyl)benzene (**1a**)¹



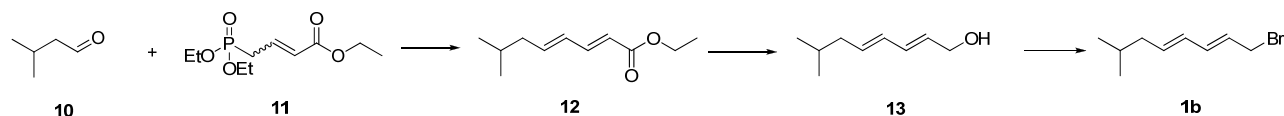
((2*E*,4*E*)-Methyl 5-phenylpenta-2,4-dienoate (8**)).** To a stirred solution of 5-phenylpenta-2,4-dienoic acid **7** (3.91 g, 22.4 mmol) in 50 mL of methanol was added HCl (20 mL, 60 mmol, 3M in methanol) at room temperature. The solution was stirred for 16 h, concentrated and purified by flash chromatography (eluent pentane/ether = 10/1) to give **8**¹ as a white solid (4.07 g, 97% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.45 – 7.21 (m, 6H), 6.87 – 6.73 (m, 2H), 5.93 (d, *J* = 15.3 Hz, 1H), 3.70 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.5, 144.8, 140.5, 136.0, 129.0, 128.8, 127.2, 126.2, 120.8, 51.6.

((2*E*,4*E*)-5-Phenylpenta-2,4-dien-1-ol (9**)).** To a stirred solution of the methyl ester **8** (4.0 g, 21.2 mmol) in 50 mL of dry DCM was added DIBAL-H (63.8 mL, 1 M in DCM, 63.8 mmol, 3 eq) over 0.5 h at –78 °C. The reaction mixture was stirred for 4 h when TLC showed full conversion. The mixture was quenched with 60 mL of saturated aqueous Rochelle salt (potassium sodium tartrate) and stirred for 30 min. The phases were separated and the aqueous layer was extracted with DCM (3 x 50 mL). The combined organic phases were dried over Na₂SO₄, filtered, concentrated and purified by flash chromatography (eluent pentane/ether = 4/1) to give **9**¹ as a white solid (3.0 g, 88% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.38 – 7.05 (m, 5H), 6.72 (dd, *J* = 15.6, 10.5 Hz, 1H), 6.49 (d, *J* = 15.6 Hz, 1H), 6.36 (dd, *J* = 15.1, 10.5 Hz, 1H), 5.90 (dt, *J* = 15.1, 5.9 Hz, 1H), 4.19 (d, *J* = 5.9 Hz, 2H), 1.31 (br, 1H); ¹³C NMR (101 MHz, CDCl₃) δ 137.1, 132.8, 132.4, 131.6, 128.6, 128.1, 127.6, 126.4, 63.5.

((1*E*,3*E*)-5-Bromopenta-1,3-dienyl)benzene (1a**).** To a stirred solution of NBS (4.17 g, 23.4 mmol, 1.3 eq) in DCM (40 mL) at –20 °C was added Me₂S (0.98 g, 1.2 mL, 28.9 mmol, 1.83 eq) slowly over 5 min. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **9** (2.5 g, 15.6 mmol) in 10 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous NH₄Cl solution (50 mL) when TLC showed full conversion and after the mixture was warmed up to room temperature, the layers were separated. The organic layer was washed with water (3 x 20 mL), dried over Na₂SO₄, filtered and concentrated to give crude **1a** as a white solid (2.83 g, 81%) which was used in the next step (asymmetric allylic alkylation) immediately due to instability.

^1H NMR (400 MHz, CDCl_3) δ 7.54 – 7.15 (m, 5H), 6.77 (dd, J = 15.6, 10.4 Hz, 1H), 6.60 (d, J = 15.6 Hz, 1H), 6.46 (dd, J = 14.8, 10.4 Hz, 1H), 6.08 – 5.90 (m, 1H), 4.11 (d, J = 8.0 Hz, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 136.7, 135.2, 134.5, 128.9, 128.7, 128.0, 127.3, 126.6, 33.4.

Synthesis of (2*E*,4*E*)-1-bromo-7-methylocta-2,4-diene (1b)



(2*E*,4*E*)-Ethyl 7-methylocta-2,4-dienoate (12). To a stirred solution of compound **11** (mixture of *E/Z* isomers, 5.0 g, 20 mmol) in 30 mL of dry THF was added LiHDMS (20 mL, 20 mmol, 1M in THF) at -78°C under nitrogen. The mixture was stirred for about 30 min when a THF solution (5 mL) of aldehyde **10** (1.72 g, 20 mmol, 1 eq) was added dropwise over 10 min. The resulting solution was stirred overnight and quenched with a saturated aqueous NH_4Cl solution (50 mL) at -78°C . The mixture was warmed up to room temperature and the layers were separated. The aqueous layer was washed with ether (3 x 30 mL) and the organic layers were dried over Na_2SO_4 , filtered and concentrated and purified by flash chromatography (eluent pentane/ether = 10/1) to give **12**² as a colorless oil (2.3 g, 62% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.25 – 7.12 (m, 1H), 6.17 – 5.94 (m, 2H), 5.72 (d, J = 15.5 Hz, 1H), 4.13 (q, J = 7.1 Hz, 2H), 2.01 – 1.97 (m, 2H), 1.66 – 1.63 (m, 1H), 1.23 (t, J = 7.1 Hz, 3H), 0.84 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.3, 145.0, 143.5, 129.4, 119.2, 60.2, 42.3, 28.3, 22.3, 14.3.

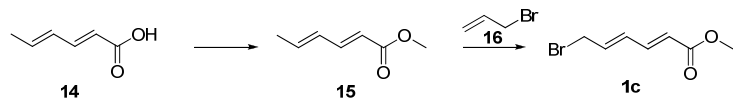
(2*E*,4*E*)-7-Methylocta-2,4-dien-1-ol (13). To a stirred solution of the ethyl ester **12** (2.0 g, 11 mmol) in 30 mL of dry DCM was added DIBAL-H (33 mL, 1 M in DCM, 33 mmol, 3 eq) over 0.5 h at -78°C . The reaction mixture was stirred for 4 h when TLC showed full conversion. The reaction mixture was quenched with 30 mL saturated aqueous Rochelle salt (potassium sodium tartrate) and stirred for 30 min. The phases were separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic phases were dried over Na_2SO_4 , filtered, concentrated and purified by flash chromatography (eluent pentane/ether = 4/1) to give **13**¹ as a colorless oil (1.5 g, 95% yield). ^1H NMR (400 MHz, CDCl_3) δ 6.23 (dd, J = 15.1, 10.4 Hz, 1H), 6.03 (dd, J = 15.1, 10.4 Hz, 1H), 5.81 – 5.63 (m, 2H), 4.16 (dd, J = 6.1, 0.9 Hz, 2H), 2.02 – 1.92 (m, 2H), 1.65 – 1.62 (m, 1H), 1.38 (br, 1H), 0.89 (d, J = 6.7 Hz, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 134.5, 132.1, 130.4, 129.3, 63.5, 42.0, 28.5, 22.3. HRMS (APCI+) calculated for $\text{C}_9\text{H}_{15}[\text{M}-\text{OH}]^+$: 123.1174, found: 123.1116.

(2*E*,4*E*)-1-Bromo-7-methylocta-2,4-diene (1b). To a stirred solution of NBS (1.07 g, 6 mmol, 1.3 eq) in DCM (20 mL) at -20°C was slowly added Me_2S (460 mg, 0.54 mL, 7.4 mmol, 1.83 eq) over a 5 min

period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **13** (560 mg, 4 mmol) in 10 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous NH₄Cl solution (50 mL) when TLC showed full conversion and after the mixture was warmed up to room temperature, the layers were separated. The organic layer was washed with water (3 x 20 mL), dried over Na₂SO₄, filtered and the solvent was concentrated to give crude **1b** as colorless oil (0.69 g, 85%) used in the next step immediately due to instability.

¹H NMR (400 MHz, CDCl₃) δ 6.32 – 6.07 (m, 1H), 5.99 – 5.88 (m, 1H), 5.78 – 5.63 (m, 2H), 4.02 – 3.85 (m, 2H), 1.96 – 1.87 (m, 2H), 1.60 – 1.57 (m, 1H), 0.82 (d, *J* = 6.7 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 136.5, 135.4, 129.8, 126.1, 42.0, 33.9, 28.4, 22.3.

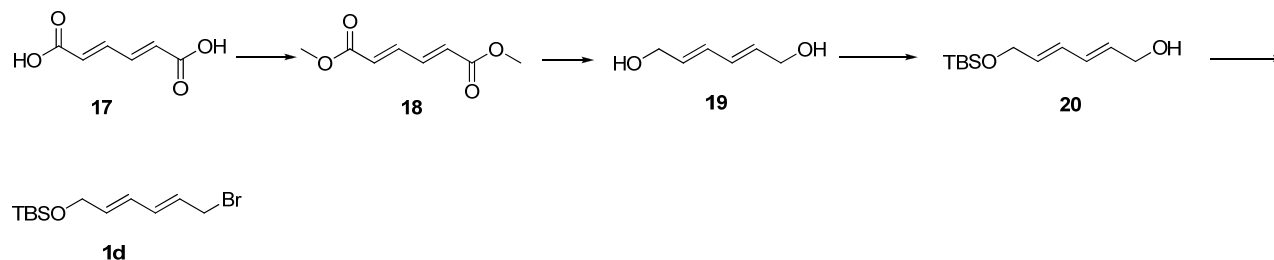
Synthesis of (2*E*,4*E*)-methyl 6-bromohexa-2,4-dienoate (**1c**)³



(2*E*,4*E*)-Methyl hexa-2,4-dienoate (15). To a stirred solution of acid **14** (4 g, 36 mmol, 1 eq) in 50 mL of methanol was added HCl (24 mL, 72 mmol, 3M in methanol, 2 eq) at room temperature. The resulting solution was stirred for 16 h, concentrated and purified by flash chromatography (eluent pentane/ether = 10/1) to give **15**⁴ as colorless oil (4.22 g, 93% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.25 – 7.10 (m, 1H), 6.19 – 5.98 (m, 2H), 5.71 (d, *J* = 15.4 Hz, 1H), 3.67 (s, 3H), 1.78 (d, *J* = 5.6 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.8, 145.2, 139.4, 129.7, 118.5, 51.4, 18.6.

(2*E*,4*E*)-Methyl 6-bromohexa-2,4-dienoate (1c). To a solution of methyl sorbate **15** (1.0 g, 8 mmol) and allyl bromide **16** (4.84 g, 40 mmol, 5 eq) in 80 mL of CH₂Cl₂ (*c* = 0.1 M) was added the Hoveyda-Grubbs-II catalyst (C₁₁H₃₈Cl₂N₂ORu, 50 mg, 0.08 mmol, 0.01 equiv) at room temperature. After stirring for 24 h, silica was added to the reaction mixture and after evaporation of the solvent, the pad of silica was loaded on top of a silica gel column and the product was quickly purified by a flash chromatography (eluent pentane/ether = 4/1) to give **1c** as a colorless oil (483 mg, 30% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.32 – 7.21 (m, 1H), 6.39 (dd, *J* = 15.0, 10.9 Hz, 1H), 6.24 (dd, *J* = 15.4, 10.9 Hz, 1H), 5.94 (d, *J* = 15.4 Hz, 1H), 4.06 – 3.99 (m, 2H), 3.75 (s, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.9, 142.8, 136.7, 131.8, 122.7, 51.7, 31.2.

Synthesis of ((2*E*,4*E*)-6-bromohexa-2,4-dienyloxy)(*tert*-butyl) dimethylsilane (**1d**)



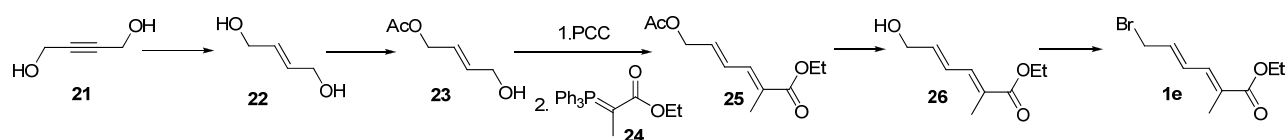
(2*E*,4*E*)-Dimethyl hexa-2,4-dienedioate (18**).** To a stirred solution of acid **17** (4.0 g, 28.1 mmol) in 50 mL of methanol was added HCl (19 mL, 57 mmol, 3M in methanol, 2 eq) at room temperature. The resulting solution was stirred for 16 h, concentrated and purified by crystallization from ether to give **18**⁵ as a white solid (4.13 g, 86% yield). ¹H NMR (400 MHz, CDCl₃) δ 7.33 – 7.21 (m, 2H), 6.21 – 6.07 (m, 2H), 3.72 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 166.3, 140.9, 128.0, 51.9.

(2*E*,4*E*)-Hexa-2,4-diene-1,6-diol (19**).** To a stirred solution of the methyl ester **18** (1.0 g, 5.94 mmol) in 30 mL of dry DCM was added DIBAL-H (36 mL, 1 M in DCM, 36 mmol, 6 eq) over 0.5 h at –78 °C. The reaction mixture was stirred for 8 h when TLC showed full conversion. The reaction mixture was quenched with 30 mL saturated aqueous Rochelle salt (potassium sodium tartrate) followed by stirring for 30 min. The phases were separated and the aqueous layer was extracted with DCM (3 x 30 mL). The combined organic phases were dried over Na₂SO₄, filtered, concentrated and purified by flash chromatography (eluent pentane/EtOAc = 2/1) to give **19**⁶ as a white solid (560 mg, 83% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.30 – 6.08 (m, 2H), 5.91 – 5.66 (m, 2H), 4.14 (t, *J* = 5.4 Hz, 4H), 1.29 (t, *J* = 5.4 Hz, 2H); ¹³C NMR (101 MHz, CDCl₃) δ 132.4, 130.4, 63.2.

(2*E*,4*E*)-6-((*tert*-Butyldimethylsilyl)oxy)hexa-2,4-dien-1-ol (20**).** To a solution of **19** (300 mg, 2.63 mmol) in dry dichloromethane (20 mL) was added imidazole (269 mg, 3.95 mmol, 1.5 eq) followed by *tert*-butyl-dimethylsilyl chloride (436 mg, 2.89 mmol, 1.1 eq), and the resulting white suspension was stirred at room temperature for 12 h. The reaction mixture was quenched with 20 mL of water and extracted with ether (3 x 20 mL). The combined organic layers were dried over Na₂SO₄, filtered, concentrated and purified by flash chromatography (eluent pentane/EtOAc = 4/1) to give **20**⁷ as a colorless oil (319 mg, 53%). ¹H NMR (400 MHz, CDCl₃) δ 6.24 – 6.11 (m, 2H), 5.81 – 5.65 (m, 2H), 4.15 (d, *J* = 4.5 Hz, 2H), 4.11 (t, *J* = 5.6 Hz, 2H), 1.50 (br, 1H), 0.84 (s, 9H), 0.00 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 133.3, 131.4, 131.0, 128.8, 63.4, 63.3, 25.9, 18.4, –5.2.

((2E,4E)-6-Bromohexa-2,4-dienyloxy)(tert-butyl) dimethylsilane (1d). To a stirred solution of NBS (267 mg, 1.5 mmol, 1.5 eq) in DCM (20 mL) at -20°C was slowly added Me_2S (115 mg, 0.14 mL, 1.85 mmol, 1.85 eq) over a 5 min period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **20** (228 mg, 1 mmol) in 5 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous NH_4Cl solution (20 mL) when TLC showed full conversion and subsequently the mixture was warmed up to room temperature and the layers separated. The organic layer was washed with water (3 x 10 mL), dried over Na_2SO_4 , filtered and concentrated to give the crude **1d** as colorless oil (248 mg, 85%) immediately used in the next step due to instability. ^1H NMR (400 MHz, CDCl_3) δ 6.29 – 6.10 (m, 2H), 5.77 (m, 2H), 4.16 (dd, $J = 5.0, 1.1$ Hz, 2H), 3.96 (d, $J = 7.9$ Hz, 2H), 0.84 (s, 9H), 0.00 (s, 6H); ^{13}C NMR (101 MHz, CDCl_3) δ 135.2, 134.4, 127.9, 127.9, 63.1, 33.3, 25.9, 18.1, – 5.3.

Synthesis of (2E,4E)-ethyl 6-bromo-2-methylhexa-2,4-dienoate (1e)



(E)-But-2-ene-1,4-diol (22). To a stirred solution of diol **21** (2.6 g, 30 mmol) in dry THF (40 mL) was added solid LiAlH_4 (1.44 g, 36 mmol, 1.2 eq) at 0°C under nitrogen. The mixture was heated to reflux for 4 h, followed by quenching with a saturated aqueous NH_4Cl solution (20 mL) at 0°C . The mixture was allowed to warm to room temperature and the phases were separated. The aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over Na_2SO_4 , filtered, concentrated and purified by flash chromatography (eluent pentane/ $\text{EtOAc} = 1/1$) to give **22**⁸ as colourless oil (660 mg, 20% yield, soluble in water). ^1H NMR (400 MHz, CDCl_3) δ 5.89 – 5.79 (m, 2H), 4.17 – 4.05 (m, 4H), 1.38 (br, 2H); ^{13}C NMR (101 MHz, CDCl_3) δ 130.5, 62.9.

(E)-4-Hydroxybut-2-en-1-yl acetate (23). To a stirred solution of but-2-ene-1,4-diol **22** (1.0 g, 11 mmol) in dry THF (20 mL) was added solid NaH (440 mg, 60% in mineral oil, 11 mmol, 1 eq) at 0°C . The mixture was stirred at room temperature for 1 h followed by the addition of a THF solution (5 mL) of acetyl chloride (863 mg, 0.81 mL, 1 eq). The reaction mixture was stirred for 3 h after which time TLC (diethyl ether) showed a mixture of starting compound, monoacetate and diacetate. H_2O (10 mL) was added, and the mixture was extracted with diethyl ether (3 x 30 mL). The combined organic phases were dried over Na_2SO_4 , filtered, concentrated and purified by flash chromatography (eluent pentane/ $\text{EtOAc} = 4/1$) to give **23**⁹ as colourless oil (930 mg, 65% yield). ^1H NMR (400 MHz, CDCl_3) δ 5.93 – 5.81 (m, 1H),

5.80 – 5.73 (m, 1H), 4.52 (dd, $J = 5.8, 1.2$ Hz, 2H), 4.12 (dd, $J = 5.0, 1.2$ Hz, 2H), 2.01 (s, 3H), 1.63 (br, 1H); ^{13}C NMR (101 MHz, CDCl_3) δ 171.6, 133.5, 125.1, 64.2, 62.7, 20.9.

(2E,4E)-Ethyl 6-acetoxy-2-methylhexa-2,4-dienoate (25). 4-Acetoxy- 2-buten-1-ol **23** (0.91 g, 7 mmol) was added to a suspension of pyridinium chlorochromate (1.81 g, 8.4 mmol) in 20 mL of DCM at 0 °C. The mixture was stirred at room temperature until TLC showed full conversion. The solids were removed by flash chromatography, washed with diethyl ether and the organic solvents were removed in vacuo to give 4-acetoxy-crotonaldehyde used immediately in the next step.

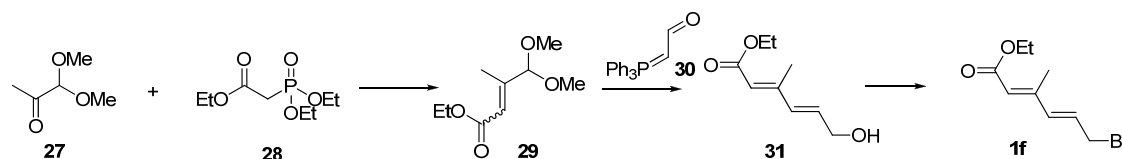
The aldehyde was dissolved in 10 mL of DCM followed by the addition of phosphorane **24** (2.54 g, 7.0 mmol) at room temperature. The solution was stirred for 30 min until TLC showed full conversion. The solvent was removed in vacuo. The product was purified by flash chromatography (eluent pentane/ether = 4/1) to give **25**⁹ as colourless oil (945 mg, 64% yield over 2 steps). ^1H NMR (400 MHz, CDCl_3) δ 7.10 (d, $J = 11.4$ Hz, 1H), 6.58 – 6.45 (m, 1H), 6.02 (dt, $J = 15.2, 6.1$ Hz, 1H), 4.62 (d, $J = 6.1$ Hz, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 2.03 (s, 3H), 1.88 (d, $J = 0.7$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H).

(2E,4E)-Ethyl 6-hydroxy-2-methylhexa-2,4-dienoate (26). K_2CO_3 (1.23 g, 8.9 mmol) was added to a solution of **25** (945 mg, 4.45 mmol) in 15 mL of ethanol at room temperature. The resulting mixture was stirred about 2 h when TLC showed full conversion. The reaction was quenched with an aqueous saturated NaCl solution (20 mL). The phases were separated and the aqueous layer was extracted with EtOAc (3 x 30 mL). The combined organic phases were dried over Na_2SO_4 , filtered, concentrated and purified by flash chromatography (eluent pentane/EtOAc = 4/1) to give **26**⁹ as colourless oil (707 mg, 93% yield). ^1H NMR (400 MHz, CDCl_3) δ 7.13 (d, $J = 11.4$ Hz, 1H), 6.53 (dd, $J = 15.2, 11.4$ Hz, 1H), 6.11 (dt, $J = 15.2, 5.2$ Hz, 1H), 4.28 – 4.20 (m, 2H), 4.15 (q, $J = 7.1$ Hz, 2H), 1.89 (d, $J = 0.7$ Hz, 3H), 1.45 (br, 1H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 168.4, 139.2, 137.1, 127.8, 125.7, 63.1, 60.6, 14.3, 12.7.

(2E,4E)-Ethyl 6-bromo-2-methylhexa-2,4-dienoate (1e). To a stirred solution of NBS (470 mg, 2.64 mmol, 1.3 eq) in DCM (20 mL) at –20 °C was slowly added Me_2S (197 mg, 0.23 mL, 3.17 mmol, 1.83 eq) over a 5 min period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **26** (300 mg, 1.76 mmol) in 5 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous NH_4Cl solution (50 mL) when TLC showed full conversion and after the mixture was warmed to room temperature, the layers were separated. The organic layer was washed with water (3 x 10 mL), dried over Na_2SO_4 , filtered and concentrated to give the crude **1e** as colorless oil (323 mg, 79%) used in the next step immediately due to instability. ^1H NMR (400 MHz, CDCl_3) δ 7.09 (dd, $J = 11.4, 0.9$

Hz, 1H), 6.59 – 6.44 (m, 1H), 6.13 (dt, $J = 15.4, 7.8$ Hz, 1H), 4.15 (q, $J = 7.1$ Hz, 2H), 4.01 (d, $J = 7.8$ Hz, 2H), 1.90 (d, $J = 1.3$ Hz, 3H), 1.24 (t, $J = 7.1$ Hz, 3H); ^{13}C NMR (101 MHz, CDCl_3) δ 167.9, 136.0, 135.1, 129.6, 129.5, 60.8, 32.0, 14.3, 12.8.

Synthesis of (2*E*,4*E*)-ethyl 6-bromo-3-methylhexa-2,4-dienoate (**1f**)



Ethyl 4,4-dimethoxy-3-methylbut-2-enoate (29). A mixture of 1,1-dimethoxyacetone **27** (5.91 g, 50 mmol) and ethyl 2-(diethoxyphosphoryl)acetate **28** (13.45 g, 60 mmol) was added dropwise to a suspension of K_2CO_3 (17.28 g) in 10 mL of water at room temperature. The reaction mixture was stirred for 16 h. The insoluble material was then removed by filtration and washed with ether. The organic phase was separated and washed with brine (50 mL). The organic layer was dried over Na_2SO_4 , filtered, concentrated and purified by flash chromatography (eluent pentane/ether) to give product **29**¹⁰ as colorless oil (8.0 g, 85%, mixture of *E* and *Z* acetal esters).

(2*E*,4*E*)-Ethyl 6-hydroxy-3-methylhexa-2,4-dienoate (31). HCl (3 N, 3.5 mL of an aq. solution) was added dropwise to a stirred solution of the above obtained esters **29** (2.0 g, 10.6 mmol) in 15 mL DCM at 0 °C. The resulting mixture was stirred for 2 h. The organic layer was separated and washed with a saturated aqueous solution of NaHCO_3 (30 mL) and brine (20 mL), dried over Na_2SO_4 , filtered and concentrated. The crude product was purified by vacuum distillation to yield the aldehyde which was used directly for the next step.

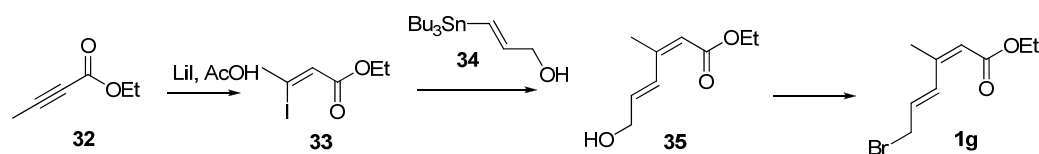
Compound **30** (3.2 g, 10.6 mmol) was added to a stirred solution of the aldehyde in DCM (10 mL) at room temperature. The reaction mixture was stirred for 15 h and subsequently concentrated. The resulting mixture was dissolved in pentane and the solids were filtered. The solution was concentrated to give the crude aldehyde which was used in the next step.

A solution of the aldehyde in 5 mL of ethanol was added to a solution of sodium borohydride (1.0 g, 25 mmol) in $\text{EtOH}/\text{H}_2\text{O}$ (1:1, 20 mL) at 0 °C. The reaction mixture was stirred at room temperature for 20 min followed by quenching with aqueous saturated NaCl . The aqueous layer was separated and extracted with Et_2O (5 x 20 mL). The combined organic layers were dried over Na_2SO_4 , filtered, concentrated and

purified by flash chromatography (eluent pentane/ether = 1/1) to give product **31**¹¹ as colorless oil (0.87 g, 50% yield over three steps). ¹H NMR (400 MHz, CDCl₃) δ 6.26 (d, *J* = 15.8 Hz, 1H), 6.17 (m, 1H), 5.71 (s, 1H), 4.24 (d, *J* = 5.2 Hz, 2H), 4.11 (q, *J* = 7.1 Hz, 2H), 2.22 (s, 3H), 1.51 (br, 1H), 1.22 (t, *J* = 7.1 Hz, 3H). ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 151.3, 134.3, 133.8, 119.7, 63.1, 59.8, 14.3, 13.8.

(2E,4E)-Ethyl 6-bromo-3-methylhexa-2,4-dienoate (1f). To a stirred solution of NBS (470 mg, 2.64 mmol, 1.3 eq) in DCM (20 mL) at –20 °C was slowly added Me₂S (197 mg, 0.23 mL, 3.17 mmol, 1.83 eq) over a 5 min period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **31** (300 mg, 1.76 mmol) in 5 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous NH₄Cl solution (50 mL) when TLC showed full conversion and subsequently the mixture was warmed up to room temperature and the layers were separated. The organic layer was washed with water (3 x 10 mL), dried over Na₂SO₄, filtered and concentrated to give the crude **1f** as colorless oil (354 mg, 86%) used in the next step immediately due to instability. ¹H NMR (400 MHz, CDCl₃) δ 6.29 – 6.13 (m, 2H), 5.73 (s, 1H), 4.11 (q, *J* = 7.1 Hz, 2H), 3.99 (d, *J* = 7.1 Hz, 2H), 2.20 (d, *J* = 1.2 Hz, 3H), 1.22 (t, *J* = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.6, 150.3, 137.6, 130.7, 121.1, 59.9, 32.0, 14.3, 13.8.

Synthesis of (2Z,4E)-ethyl 6-bromo-3-methylhexa-2,4-dienoate (1g)



(Z)-Ethyl 3-iodobut-2-enoate (33). To a mixture of ethyl but-2-ynoate **32** (2.34 g, 20 mmol) and lithium iodide (4.4 g, 32 mmol, 1.6 eq) was added acetic acid (6 mL) at room temperature. The reaction mixture was heated to 70 °C and stirred for 16 h followed by dilution with ether (50 mL). The organic phase was washed with water (20 mL), saturated aqueous NaHCO₃ (20 mL), and saturated aqueous Na₂S₂O₃ (20 mL), dried over Na₂SO₄, filtered and concentrated and purified by flash chromatography (eluent pentane/ether = 10/1) to give product **33**¹² as a colorless oil (2.1 g, 88% yield). ¹H NMR (400 MHz, CDCl₃) δ 6.29 (q, *J* = 1.4 Hz, 1H), 4.22 (q, *J* = 7.1 Hz, 2H), 2.73 (d, *J* = 1.4 Hz, 3H), 1.29 (t, *J* = 7.1 Hz, 3H).

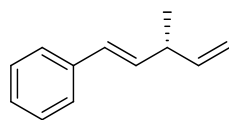
(2Z,4E)-Ethyl 6-hydroxy-3-methylhexa-2,4-dienoate (35). A solution of $\text{Pd}_2(\text{dba})_3$ (45 mg, 0.005 mmol) in 20 mL of NMP was treated with triphenyl arsine (59 mg, 0.2 mmol) at room temperature. The solution was stirred for 10 min followed by the addition of a solution of iodide **33** (466 mg, 1.94 mmol) in 5 mL of NMP. The solution was further stirred for 10 min followed by the addition of a solution of stannane **34**¹³ (674 mg, 1.94 mmol) in 5 mL of NMP. The reaction mixture was stirred for 16 h followed by quenching with saturated aqueous potassium fluoride solution (20 mL). The reaction mixture was diluted with diethyl ether (20 mL). The organic layer was separated and washed with saturated aqueous potassium fluoride solution (10 mL), dried over Na_2SO_4 , filtered and concentrated. The product was purified by column chromatography (eluent pentane/ether = 2/1) to give **35** as a colourless oil (252 mg, 76%). ¹H NMR (400 MHz, CDCl_3) δ 7.75 (dd, J = 16.0, 0.7 Hz, 1H), 6.23 (dt, J = 16.0, 5.6 Hz, 1H), 5.71 (s, 1H), 4.32 (td, J = 5.6, 1.4 Hz, 2H), 4.16 (q, J = 7.1 Hz, 2H), 2.02 (d, J = 1.3 Hz, 3H), 1.63 (br, 1H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl_3) δ 166.2, 150.0, 135.8, 127.8, 117.9, 63.6, 59.8, 21.0, 14.3. HRMS (APCI+) calculated for $\text{C}_9\text{H}_{13}\text{O}_2[\text{M}-\text{OH}]^+$:153.0910, found:153.0909.

(2Z,4E)-Ethyl 6-bromo-3-methylhexa-2,4-dienoate (1g). To a stirred solution of NBS (313 mg, 1.76 mmol, 1.3 eq) in DCM (20 mL) at -20°C was slowly added Me_2S (132 mg, 0.16 mL, 2.12 mmol, 1.83 eq) over a 5 min period. The reaction mixture was stirred for 15 min before a solution of allylic alcohol **35** (200 mg, 1.18 mmol) in 5 mL of DCM was added dropwise over 10 min. The mixture was quenched with a saturated aqueous NH_4Cl solution (50 mL) after TLC showed full conversion and subsequently the mixture was warmed up to room temperature and the layers were separated. The organic layer was washed with water (3 x 10 mL), dried over anhydrous Na_2SO_4 , filtered and concentrated to give the crude **1g** as colorless oil (214 mg, 78%) used in the next step immediately due to instability. ¹H NMR (400 MHz, CDCl_3) δ 7.80 (dd, J = 15.6, 0.9 Hz, 1H), 6.23 (dt, J = 15.6, 7.8 Hz, 1H), 5.72 (s, 1H), 4.16 (q, J = 7.1 Hz, 2H), 4.10 (dd, J = 7.8, 0.9 Hz, 2H), 2.00 (d, J = 1.3 Hz, 3H), 1.28 (t, J = 7.1 Hz, 3H); ¹³C NMR (101 MHz, CDCl_3) δ 165.9, 149.0, 132.0, 131.1, 119.2, 59.9, 32.6, 20.8, 14.3.

General procedure for the copper-catalyzed allylic alkylation of an allylic bromide with organomagnesium reagents

A Schlenk tube equipped with septum and stirring bar was charged with CuBr•SMe₂ (0.0125 mmol, 2.6 mg, 5 mol%) and the appropriate ligand (0.015 mmol, 6 mol%). Dry dichloromethane (3 mL) was added and the solution was stirred under nitrogen at room temperature for 15 min and cooled to –80 °C. Then, the corresponding organomagnesium reagent (0.3 mmol, 1.2 eq) was added under nitrogen. Allylic bromide (0.25 mmol) was dissolved in 1 mL of DCM and added dropwise to the reaction mixture over 1 h using a syringe pump. The reaction was quenched after overnight with a saturated aqueous NH₄Cl solution (2 mL) and the mixture was warmed up to room temperature, diluted with ether and the layers were separated. The aqueous layer was extracted with dichloromethane (3 x 5 mL) and the combined organic layers were dried over anhydrous Na₂SO₄, filtered and carefully concentrated (note: several products are highly volatile). The crude product was purified by flash chromatography on silica gel using different mixtures of n-pentane: Et₂O as the eluent.

Note: Gas chromatography analysis was carried out to determine the S_N2':S_N2 ratio's and ee's on a sample obtained after aqueous extraction with dichloromethane, which has been passed through a short plug of silica gel to remove transition metal residues.



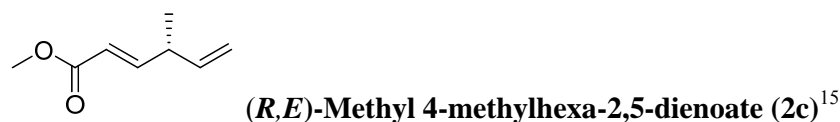
(*R,E*)-(3-Methylpenta-1,4-dienyl)benzene (**2a**)

The title compound was prepared from **1a** (55 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography (SiO₂, Pentane) afforded product (26 mg, 66% yield, 99% *ee*) as a colourless oil as a mixture of two regioisomers **2a/3a** (S_N2'/S_N2) in 95:5 ratio (determined by ¹H NMR at 20 °C and GC). ¹H NMR (400 MHz, CDCl₃) δ 7.40 – 7.14 (m, 5H), 6.39 (d, *J* = 16.0 Hz, 1H), 6.18 (dd, *J* = 16.0, 7.0 Hz, 1H), 5.88 (ddd, *J* = 17.0, 10.3, 6.5 Hz, 1H), 5.05 (m, 2H), 3.11 – 2.99 (m, 1H), 1.21 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 142.4, 137.6, 134.3, 128.6, 128.5, 127.0, 126.1, 113.3, 40.6, 19.8. HRMS (APCI+) calculated for C₁₂H₁₅:159.1168, found: 159.1157. [α]_D²⁰ = –56.5 (*c* = 2.3, CHCl₃), [Lit. ¹⁴ (*S* isomer, *er* = 96:4) [α]_D²⁰ = +55 (*c* = 0.87, CHCl₃)]. Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 80 °C for 80 min, then 1°C/min to 140°C (hold for 5 min), then 10°C/min to 180°C (final temp), retention times (min.): 25.8 (major) and 26.9 (minor); retention time **3a**: 72.0 min.

In analogy to this result, the absolute configuration of the other products is assumed to be (*R*).



The title compound was prepared from **1b** (50 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography (SiO₂, Pentane) afforded product (11 mg, 32% yield, 99% *ee*) as a colourless oil as a mixture of two regioisomers **2b/3b** (S_N2'/S_N2) in 96:4 ratio (determined by ¹H NMR at 20 °C and GC). ¹H NMR (400 MHz, CDCl₃) δ 5.80 – 5.66 (m, 1H), 5.38 – 5.23 (m, 2H), 4.97 – 4.81 (m, 2H), 2.77 – 2.73 (m, 1H), 1.82 (dd, *J* = 9.7, 3.6 Hz, 2H), 1.55 – 1.50 (m, 1H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.80 (d, *J* = 6.6 Hz, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 143.4, 135.0, 128.0, 112.4, 41.9, 40.3, 28.4, 22.2, 20.0. HRMS (APCI+) calculated for C₇H₁₁ [M-*iso*-propyl]⁺: 95.0861, found: 95.0814. [α]_D²⁰ = +4.8 (*c* = 0.25, CHCl₃). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 60 °C for 20 min, then 0.5°C/min to 100°C (hold for 10 min), then 1°C/min to 140°C (final temp), retention times (min.): 15.1 (major) and 15.5 (minor); retention time **3b**: 34.6 min.

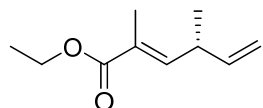


The title compound was prepared from **1c** (51 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography (SiO₂, Pentane/Et₂O = 10/1) afforded product (15 mg, 43% yield, 97% *ee*) as a colorless oil as a mixture of two regioisomers **2c/3c** (S_N2'/S_N2) in 94:6 ratio (determined by ¹H NMR at 20 °C and GC). ¹H NMR (400 MHz, CDCl₃) δ 6.86 (dd, *J* = 15.7, 6.9 Hz, 1H), 5.79 – 5.63 (m, 2H), 5.05 – 4.94 (m, 2H), 3.66 (s, 3H), 3.02 – 2.87 (m, 1H), 1.10 (d, *J* = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.1, 152.1, 140.0, 119.7, 114.8, 51.4, 40.0, 18.8. [α]_D²⁰ = –20 (*c* = 0.65, CHCl₃). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 60 °C for 20 min, then 0.5°C/min to 100°C (hold for 10 min), then 1°C/min to 140°C (final temp), retention times (min.): 35.9 (major) and 37.6 (minor); retention time **3c**: 64.0 min.



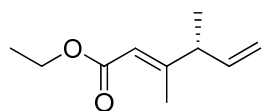
The title compound was prepared from **1d** (73 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography (SiO₂, Pentane/Et₂O = 10/1) afforded product (52 mg, 92% yield, 99% *ee*) as a colorless oil as a mixture of two regioisomers **2d/3d** (S_N2'/S_N2) in 91:9 ratio (determined by ¹H NMR at 20 °C and GC). ¹H NMR (400

MHz, CDCl₃) δ 5.72 (ddd, J = 17.1, 10.3, 6.6 Hz, 1H), 5.58 – 5.39 (m, 2H), 4.91 (m, 2H), 4.08 (dt, J = 4.7, 1.0 Hz, 2H), 2.87 – 2.72 (m, 1H), 1.03 (d, J = 6.9 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 142.6, 134.5, 128.2, 112.9, 64.0, 39.9, 26.0, 19.6, 18.4, –5.1. HRMS (ESI+) calculated for C₁₃H₂₇OSi: 227.1826, found: 227.1820. $[\alpha]_D^{20}$ = –4.4 (c = 2.5, CHCl₃). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 80 °C for 80 min, then 1 °C/min to 140 °C (hold for 5 min), then 10 °C/min to 180 °C (final temp), retention times (min.): 23.6 (major) and 24.4 (minor); retention time **3d**: 48.2 min.



(R,E)-Ethyl 2,4-dimethylhexa-2,5-dienoate (2e)

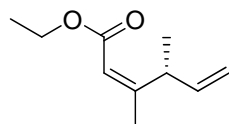
The title compound was prepared from **1e** (58 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography (SiO₂, Pentane/Et₂O = 10/1) afforded product (38 mg, 90% yield, 98% *ee*) as a colorless oil as a mixture of two regioisomers **2e/3e** (S_N2'/S_N2) in 97:3 ratio (determined by ¹H NMR at 20 °C and GC). ¹H NMR (400 MHz, CDCl₃) δ 6.51 (dd, J = 9.6, 1.4 Hz, 1H), 5.69 (ddd, J = 16.6, 10.3, 6.4 Hz, 1H), 5.02 – 4.87 (m, 2H), 4.12 (q, J = 7.1 Hz, 2H), 3.16 – 3.10 (m, 1H), 1.79 (d, J = 1.3 Hz, 3H), 1.23 (t, J = 7.1 Hz, 3H), 1.07 (d, J = 6.8 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 168.3, 144.5, 140.6, 127.0, 113.7, 60.5, 37.0, 19.7, 14.3, 12.4. HRMS (APCI+) calculated for C₁₀H₁₇O₂: 169.1223, found: 169.1219. $[\alpha]_D^{20}$ = –2.8 (c = 1.85, CHCl₃). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 60 °C for 20 min, then 0.5 °C/min to 100 °C (hold for 10 min), then 1 °C/min to 140 °C (final temp), retention times (min.): 54.6 (major) and 55.8 (minor); retention time **3e**: 86.3 min.



(R,E)-Ethyl 3,4-dimethylhexa-2,5-dienoate (2f)

The title compound was prepared from **1f** (58 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography (SiO₂, Pentane/Et₂O = 10/1) afforded product (31 mg, 74% yield, 98% *ee*) as a colorless oil as a mixture of two regioisomers **2f/3f** (S_N2'/S_N2) in 95:5 ratio (determined by ¹H NMR at 20 °C and GC). ¹H NMR (400 MHz, CDCl₃) δ 5.75 – 5.60 (m, 2H), 5.05 – 4.96 (m, 2H), 4.09 (q, J = 7.1 Hz, 2H), 2.89 – 2.77 (m, 1H), 2.05 (d, J = 1.3 Hz, 3H), 1.21 (t, J = 7.1 Hz, 3H), 1.10 (d, J = 6.9 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 167.0, 162.2, 140.3, 115.2, 115.0, 59.6, 47.2, 17.8, 16.8, 14.3. HRMS (APCI+) calculated for C₁₀H₁₇O₂: 169.1223, found: 169.1220. $[\alpha]_D^{20}$ = +19.0 (c = 0.6, CHCl₃). Enantiomeric excess was

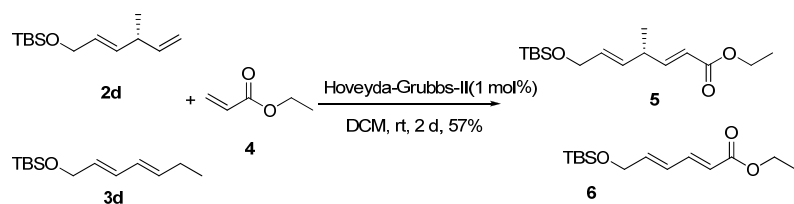
determined by HPLC analysis (Chiralpak OD-H: 0.5 mL/min, n-heptane, 40 °C isotherm, 214 nm), retention times: 54.2 min (major), 57.9 min (minor).



(*R,Z*)-Ethyl 3,4-dimethylhexa-2,5-dienoate (2g)

The title compound was prepared from **1g** (58 mg, 0.25 mmol) following the general procedure for the copper-catalyzed asymmetric allylic alkylation. Purification by column chromatography (SiO₂, Pentane/Et₂O = 10/1) afforded product (**2g**, 32 mg, 74% yield with trace of ether, 99% *ee*) as a colorless oil as a mixture of two regioisomers **2g/3g** (*S_N2'*/*S_N2*) in 96:4 ratio (determined by ¹H NMR at 20 °C and GC). ¹H NMR (400 MHz, CDCl₃) δ 5.77 (ddd, *J* = 16.4, 10.4, 6.0 Hz, 1H), 5.58 (s, 1H), 5.10 – 4.92 (m, 2H), 4.63 – 4.50 (m, 1H), 4.08 (q, *J* = 7.1 Hz, 2H), 1.71 (d, *J* = 1.0 Hz, 3H), 1.21 (t, *J* = 7.1 Hz, 3H), 1.08 (d, *J* = 7.0 Hz, 3H); ¹³C NMR (101 MHz, CDCl₃) δ 166.1, 162.0, 140.4, 116.1, 114.3, 59.5, 37.9, 20.0, 17.1, 14.3. HRMS (APCI+) calculated for C₁₀H₁₇O₂:169.1223, found: 169.1222. [α]_D²⁰ = +130.1 (*c* = 1.5, CH₂Cl₂). Enantiomeric excess was determined by chiral GC analysis, CP-Chiralsil-Dex-CB (25 m x 0.25 mm), initial temperature 60 °C for 20 min, then 0.5°C/min to 100°C (hold for 10 min), then 1°C/min to 140°C (final temp), retention times (min): 56.1 (major) and 56.5 (minor); retention time **3g**: 80.6 min.

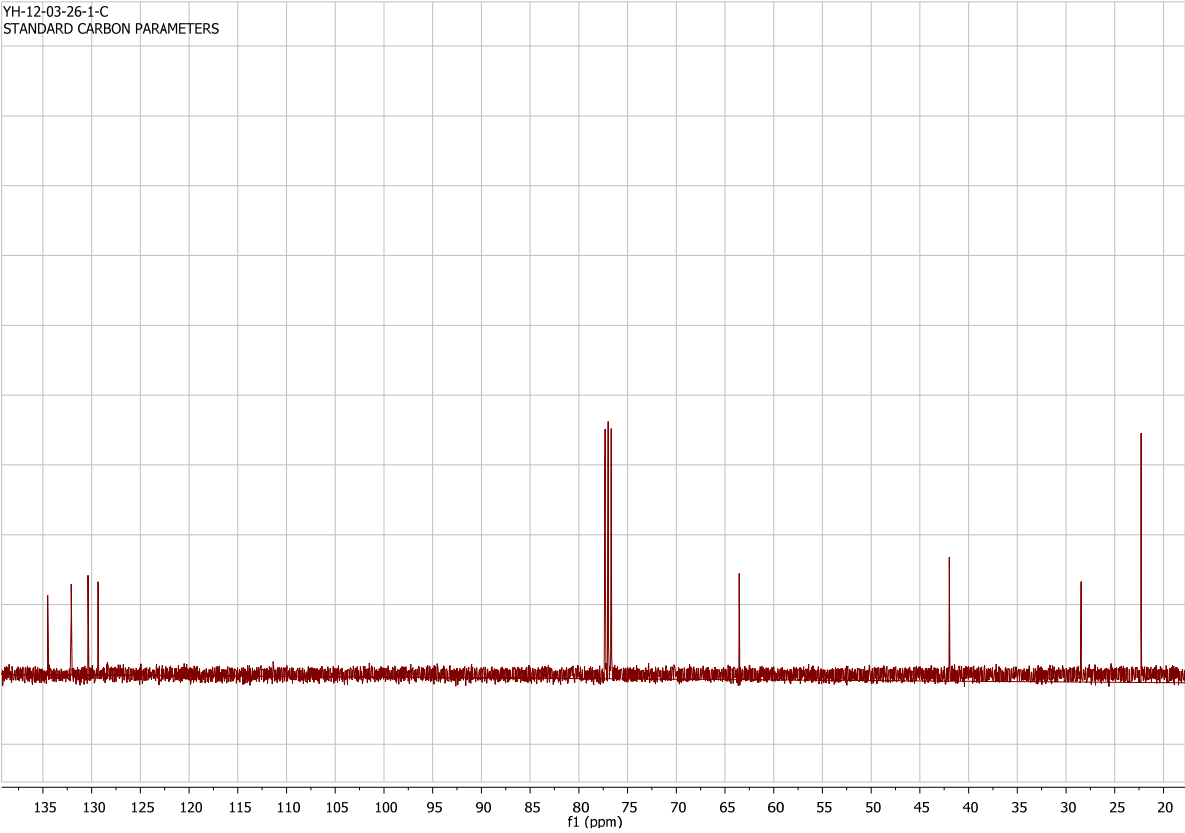
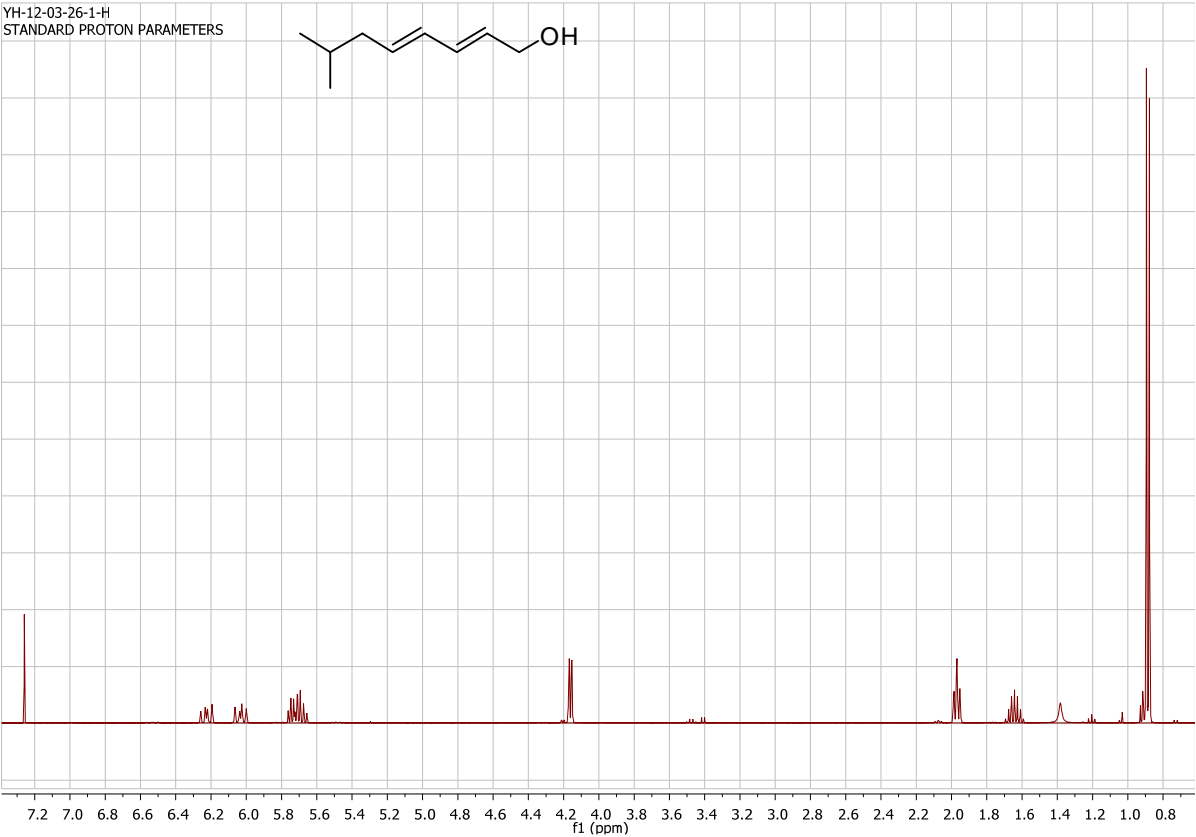
Cross metathesis between **2d** and **4**

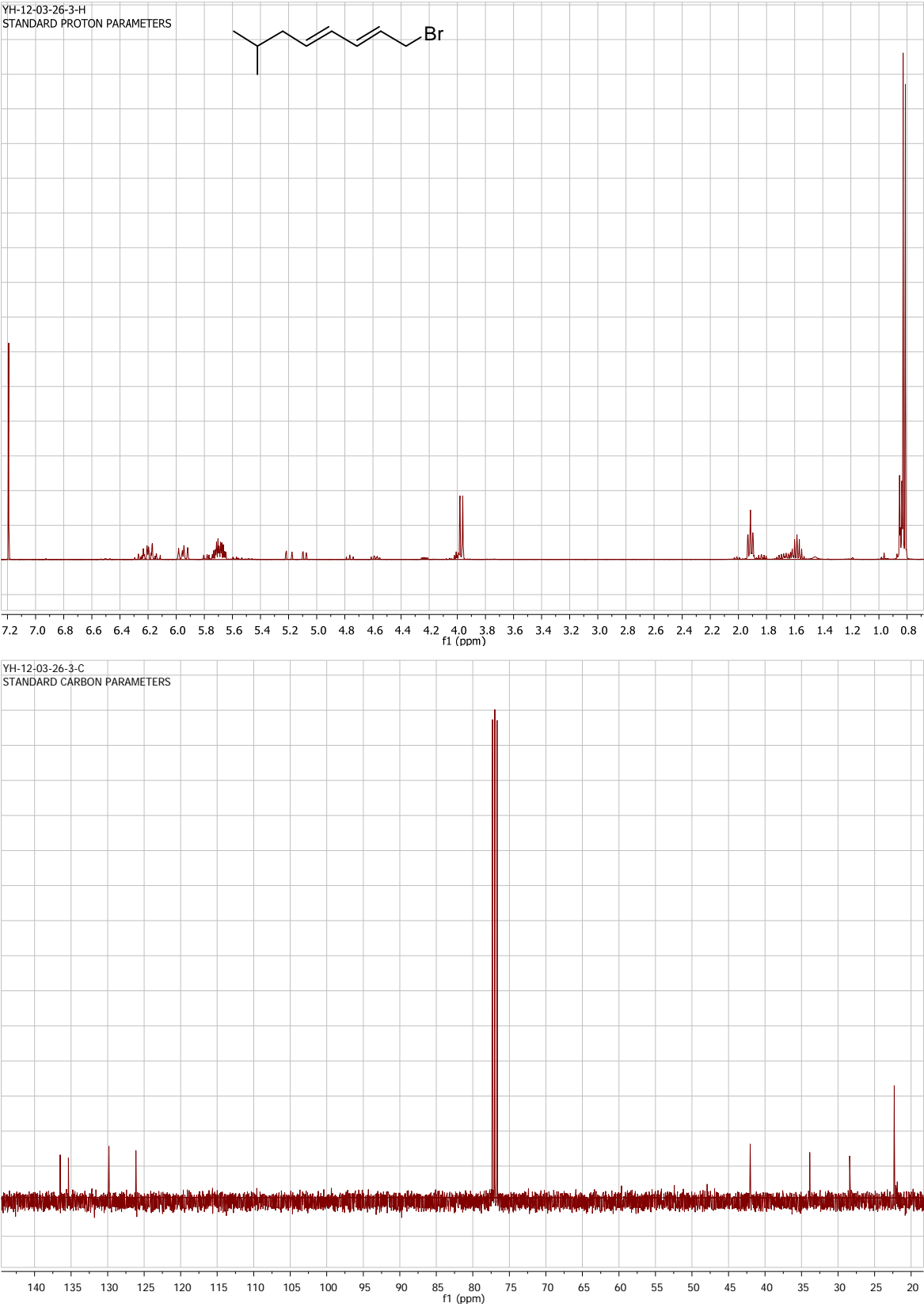


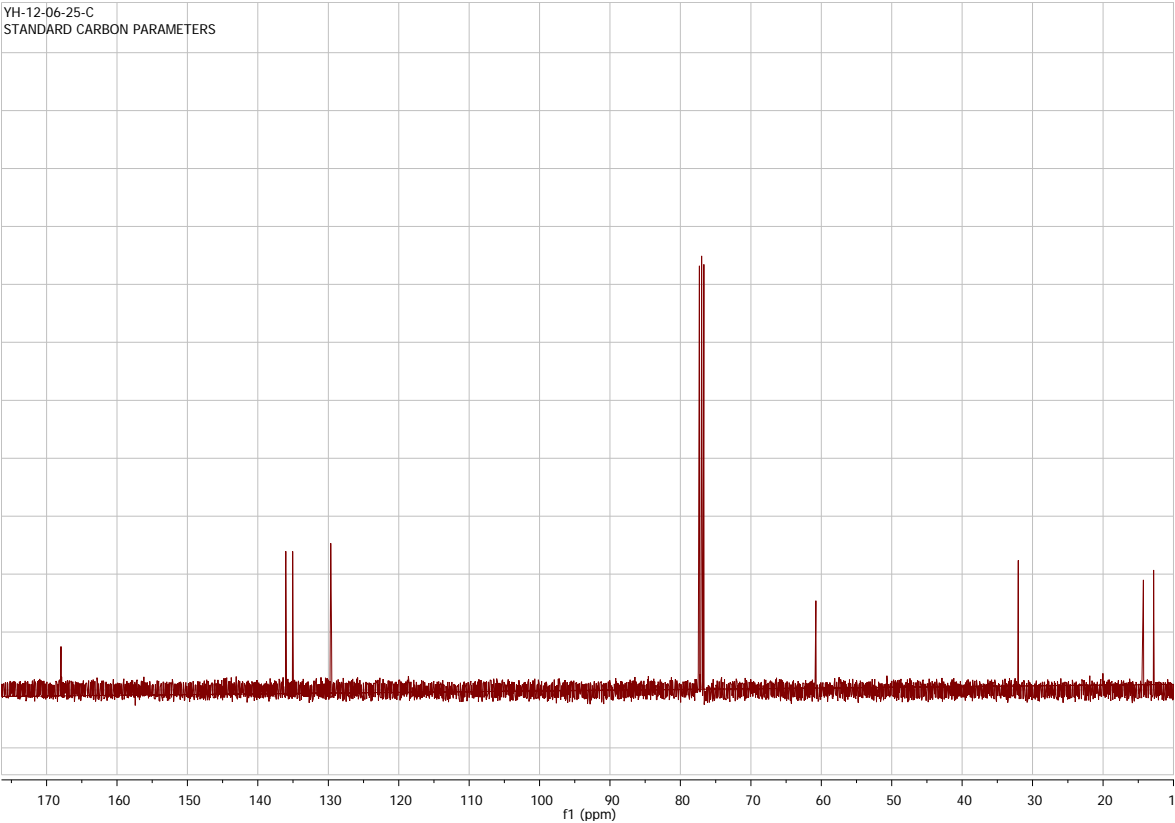
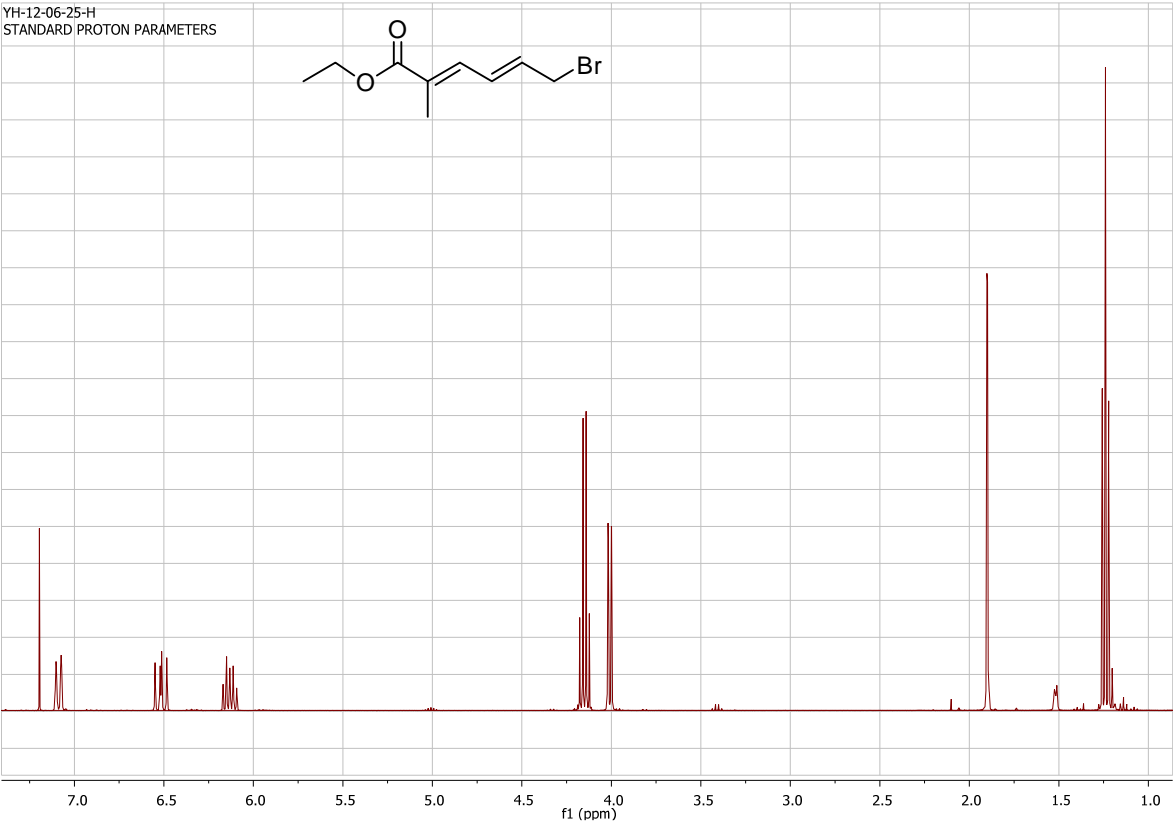
(*S,2E,5E*)-Ethyl 7-((*tert*-butyldimethylsilyl)oxy)-4-methylhepta-2,5-dienoate (5**).** To a stirred solution of compound **2d/3d** (20 mg, 0.088 mmol, 91/9) in 4 mL of dry DCM was added ethyl acrylate **4** (9 mg, 0.09 mmol) and Hoveyda–Grubbs second-generation catalyst¹⁶ (0.6 mg, 0.00088 mmol, 1 mol%) under a nitrogen atmosphere at room temperature. The reaction mixture was stirred for 2 d and the product was purified by flash chromatography (pentane/Et₂O = 10/1) to give **5** as a colorless oil (15 mg, 57%) which was contaminated by trace of compound **6**. ¹H NMR (400 MHz, CDCl₃) δ 6.84 (dd, *J* = 15.7, 6.9 Hz, 1H), 5.72 (dd, *J* = 15.7, 1.4 Hz, 1H), 5.55 – 5.44 (m, 2H), 4.14 – 4.07 (m, 4H), 2.99 – 2.94 (m, 1H), 1.22 (t, *J* = 7.1 Hz, 3H), 1.10 (d, *J* = 6.9 Hz, 3H), 0.84 (s, 9H), 0.00 (s, 6H); ¹³C NMR (101 MHz, CDCl₃) δ 166.8, 152.1, 132.0, 129.8, 119.9, 63.6, 60.2, 38.7, 26.0, 19.1, 18.4, 14.3, -5.2. HRMS (APCI+) calculated for C₁₆H₃₁O₃Si:299.2042, found: 299.2037. [α]_D²⁰ = +8.2 (*c* = 0.7, CH₂Cl₂).

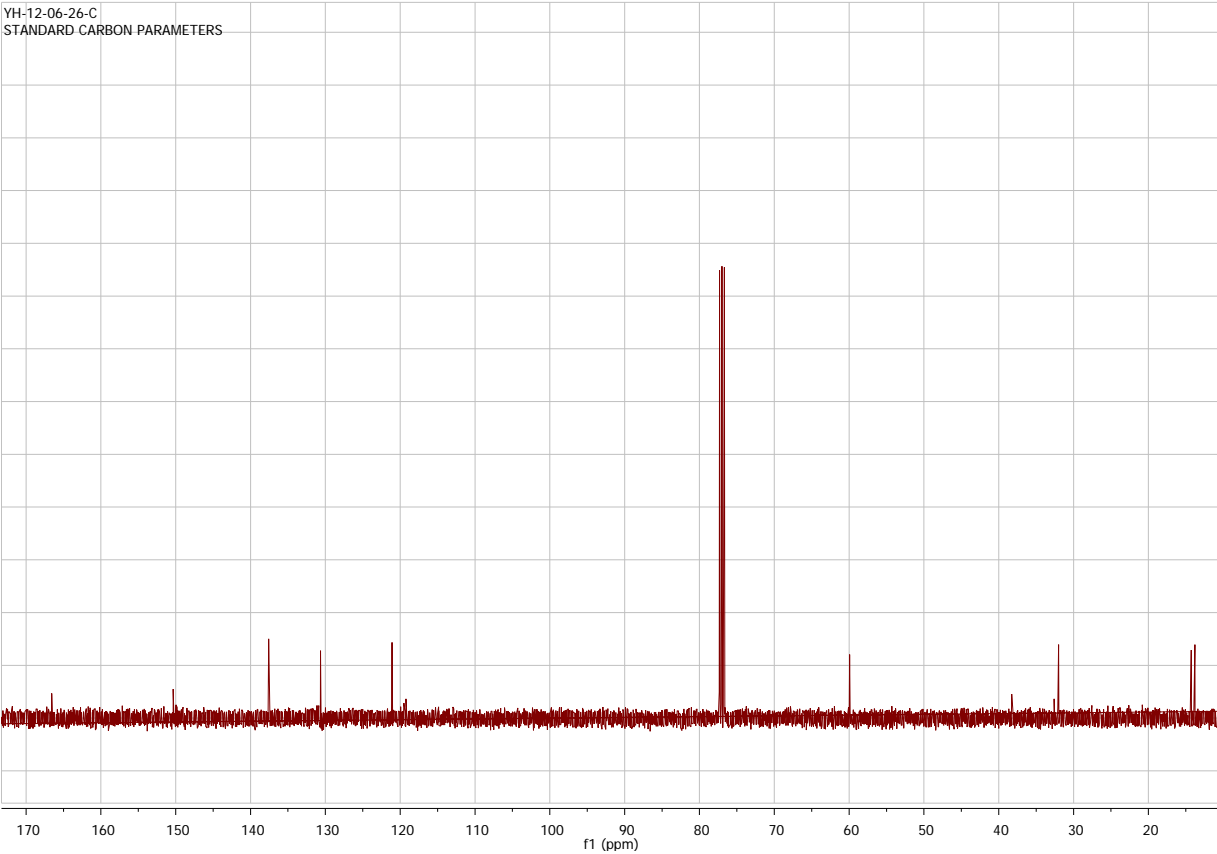
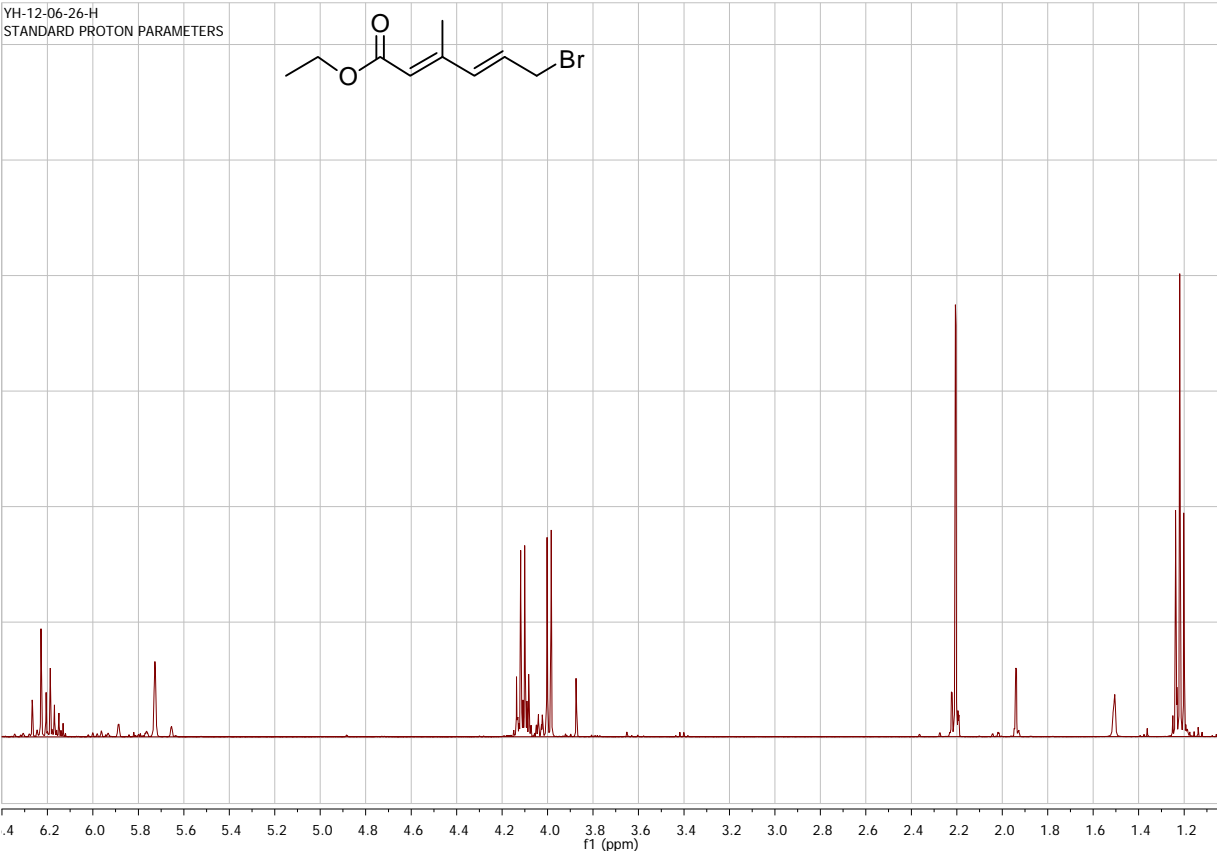
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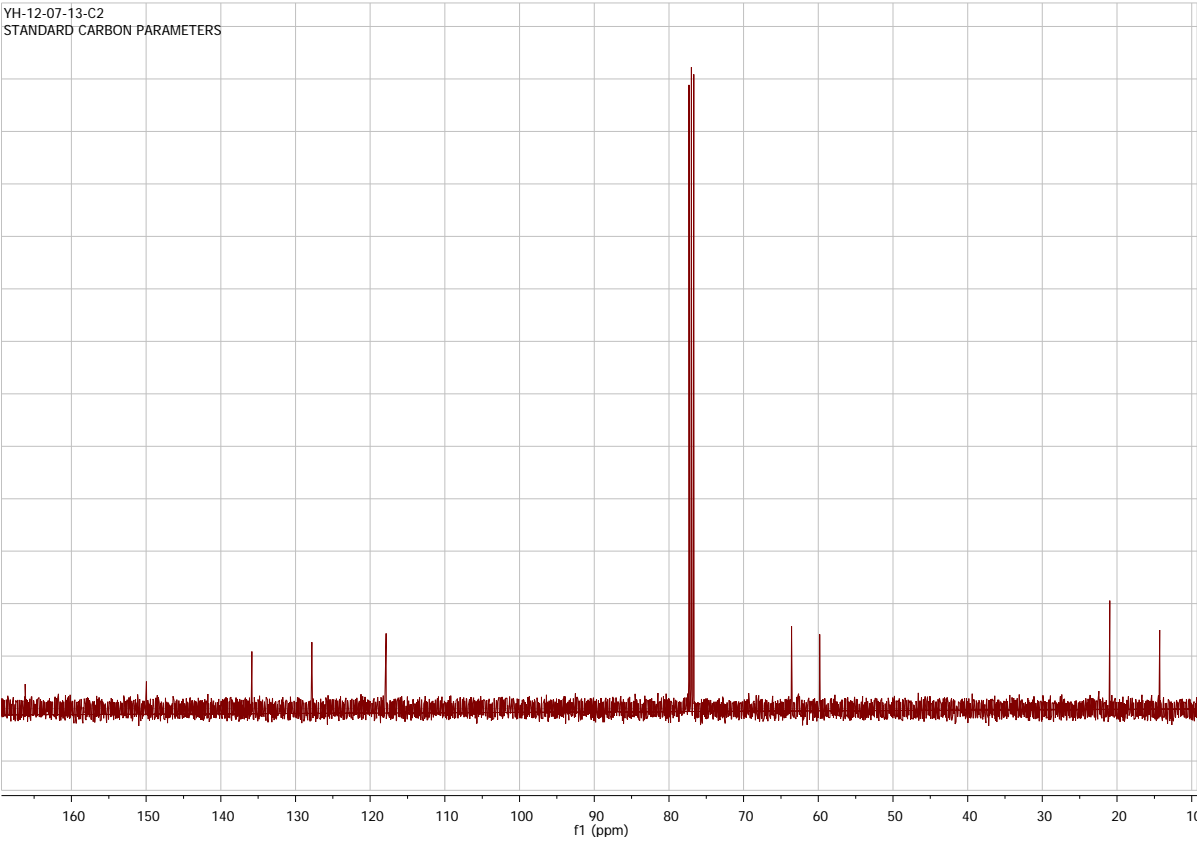
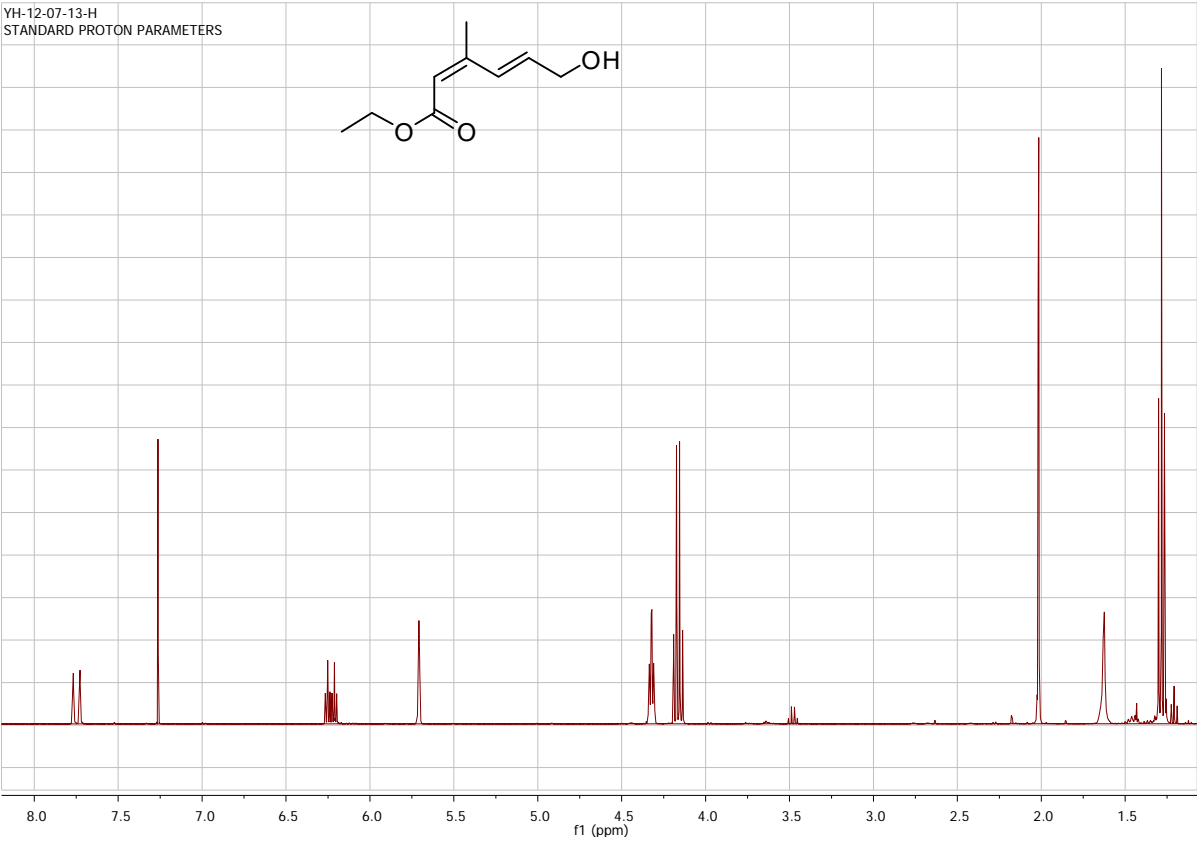
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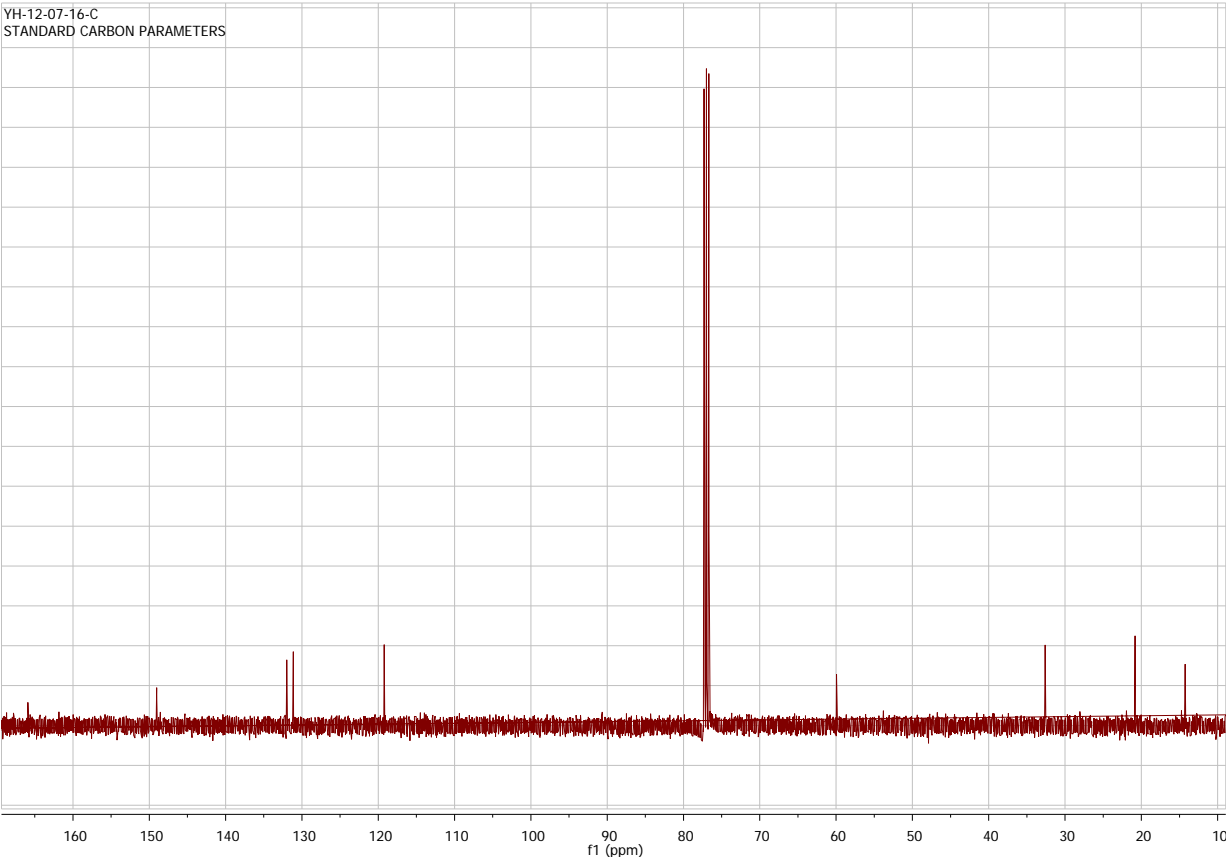
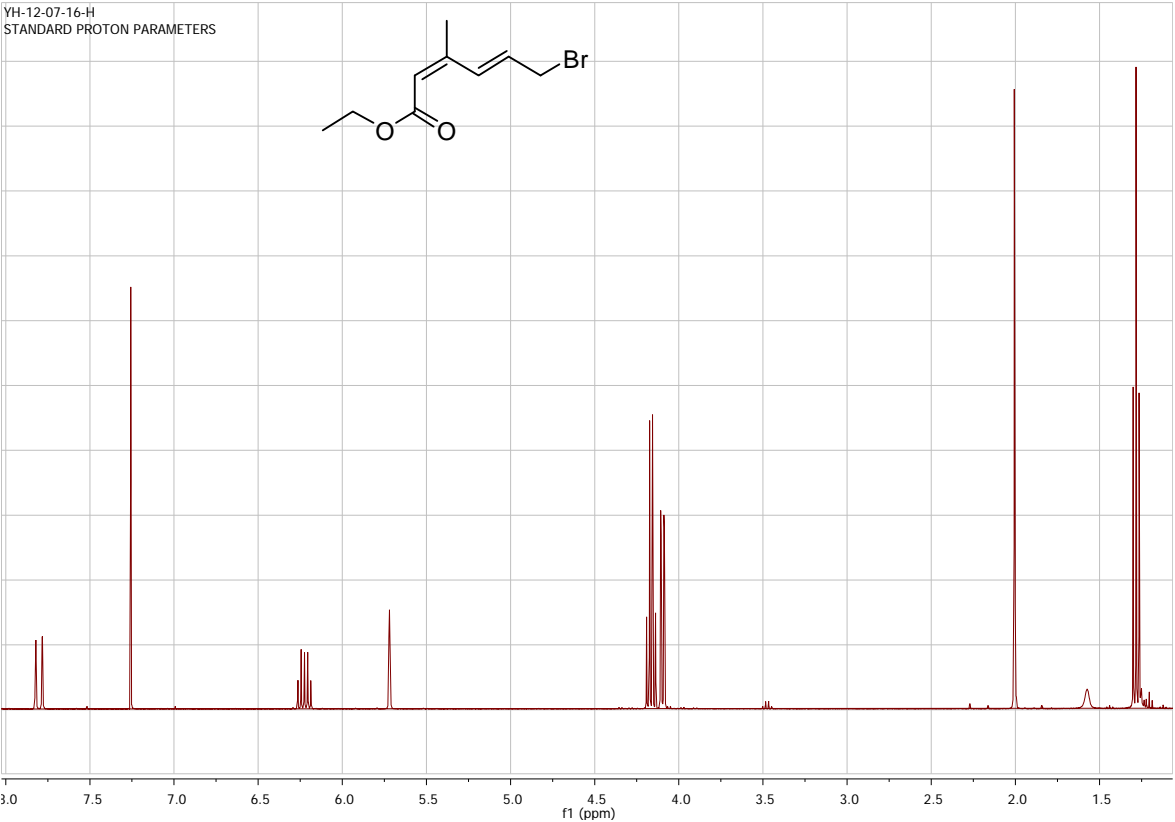


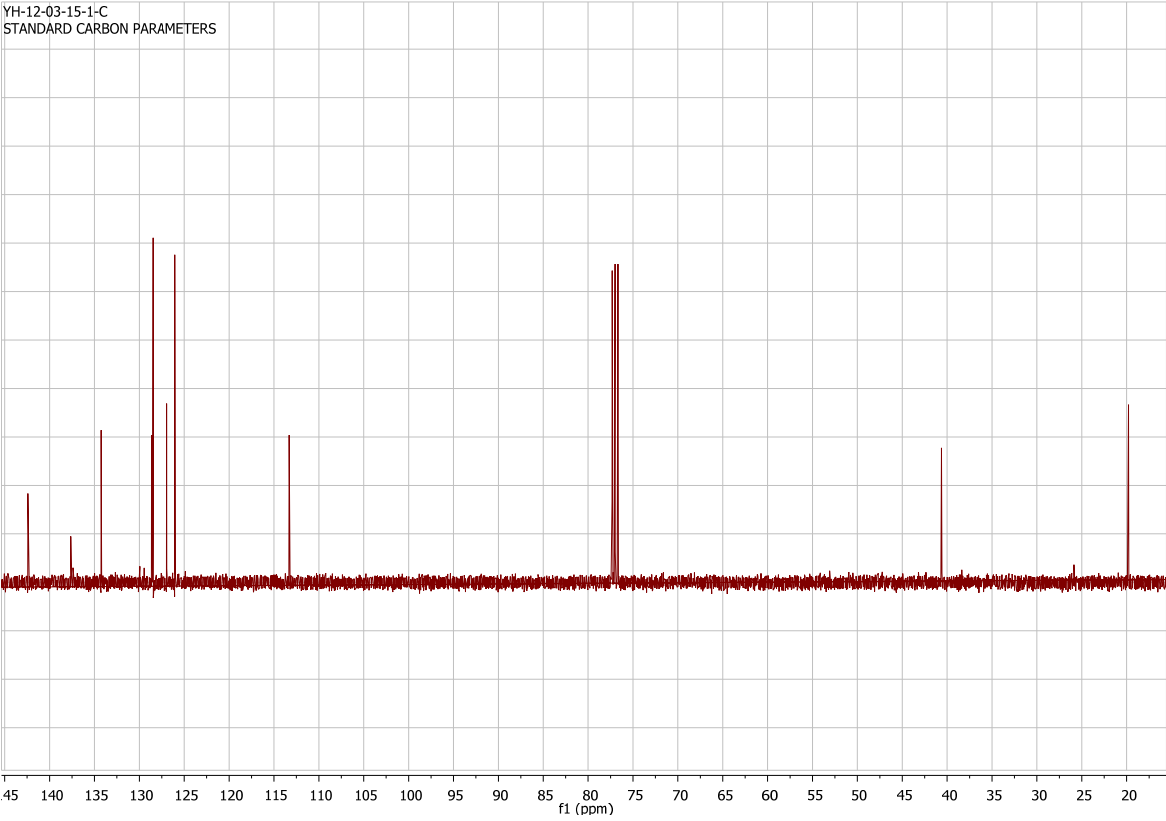
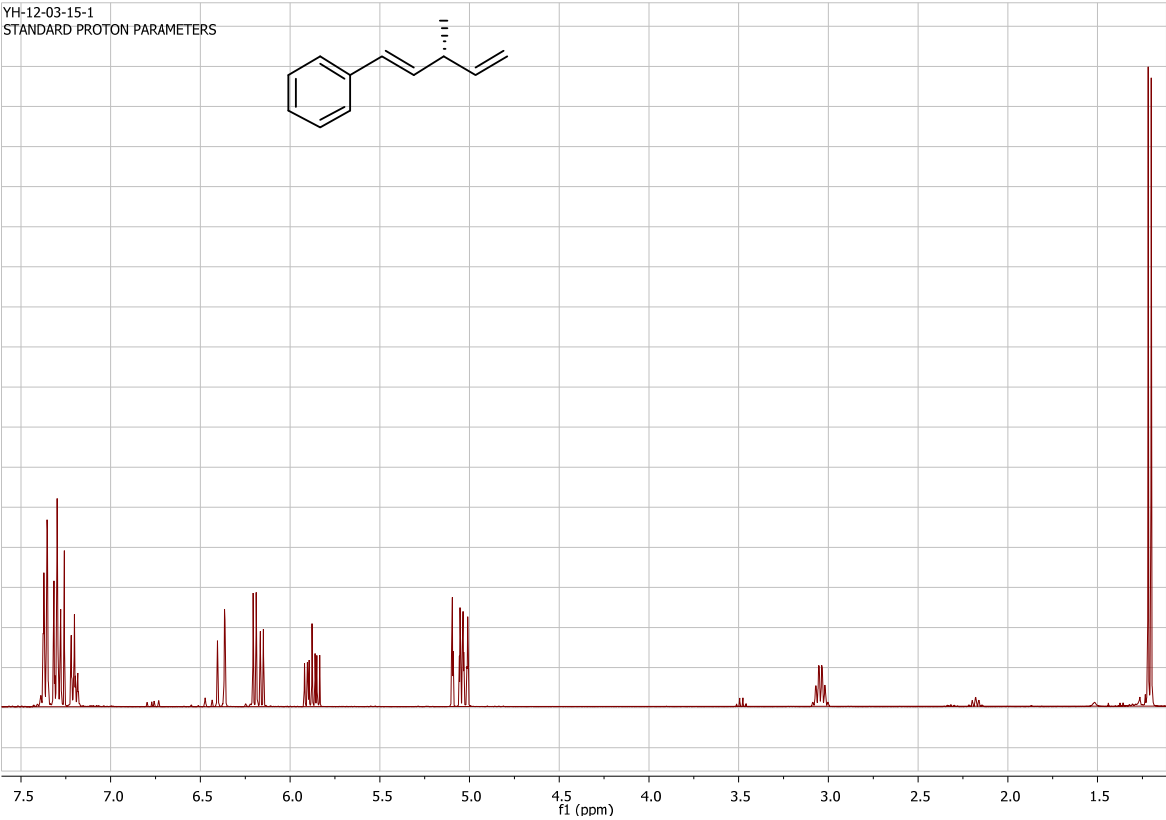


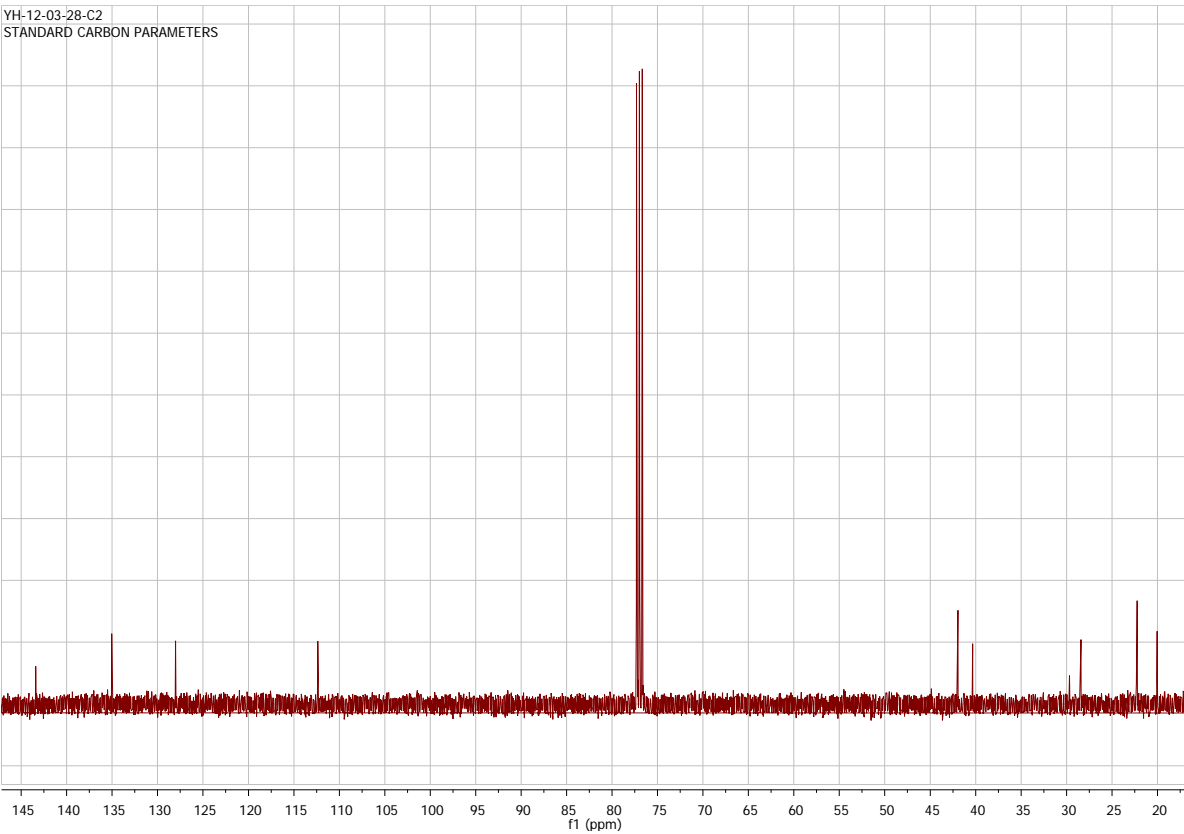
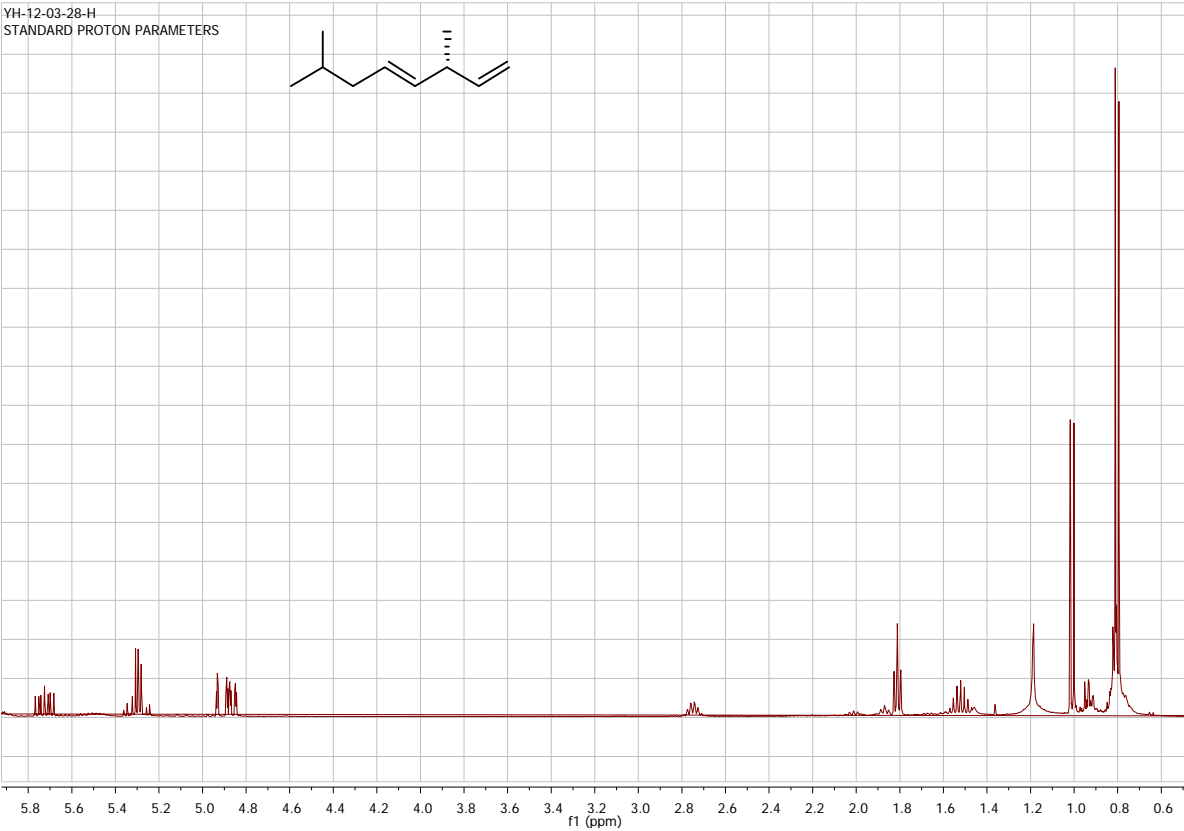


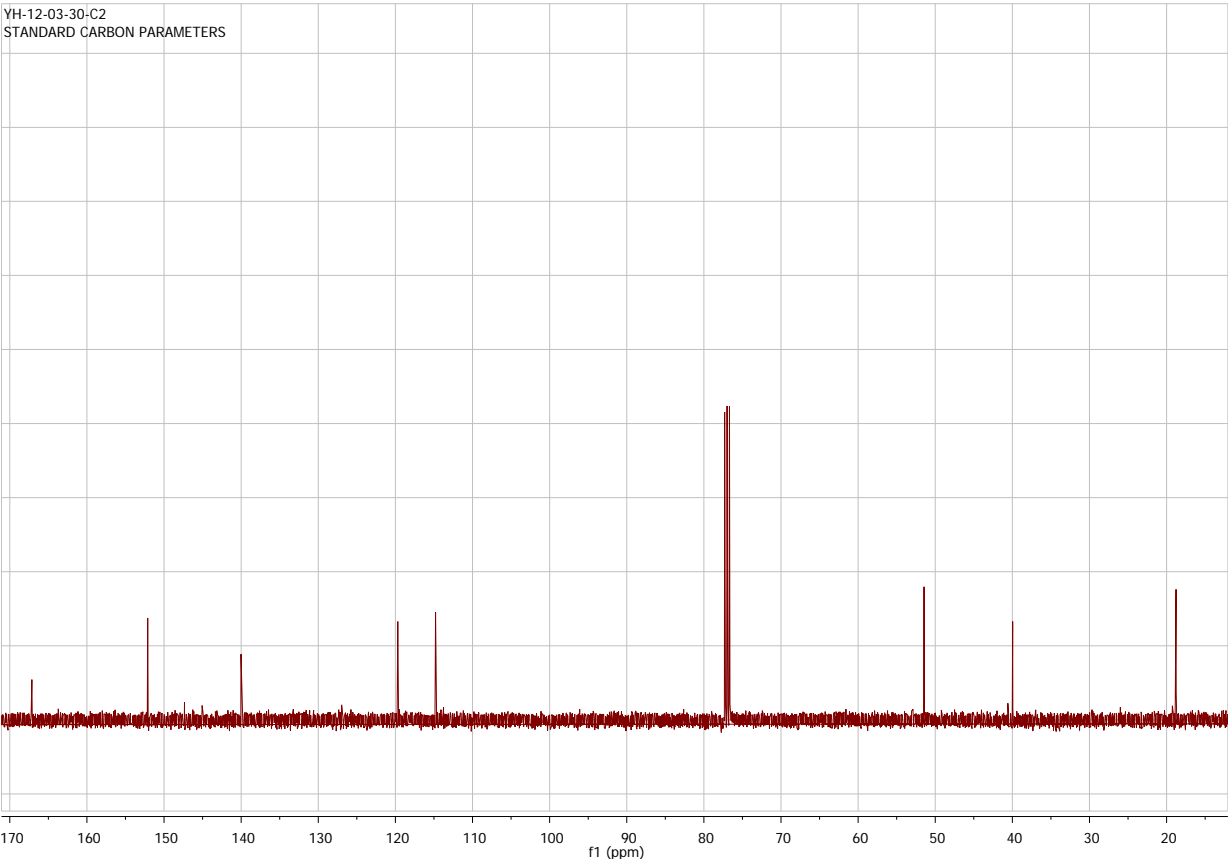
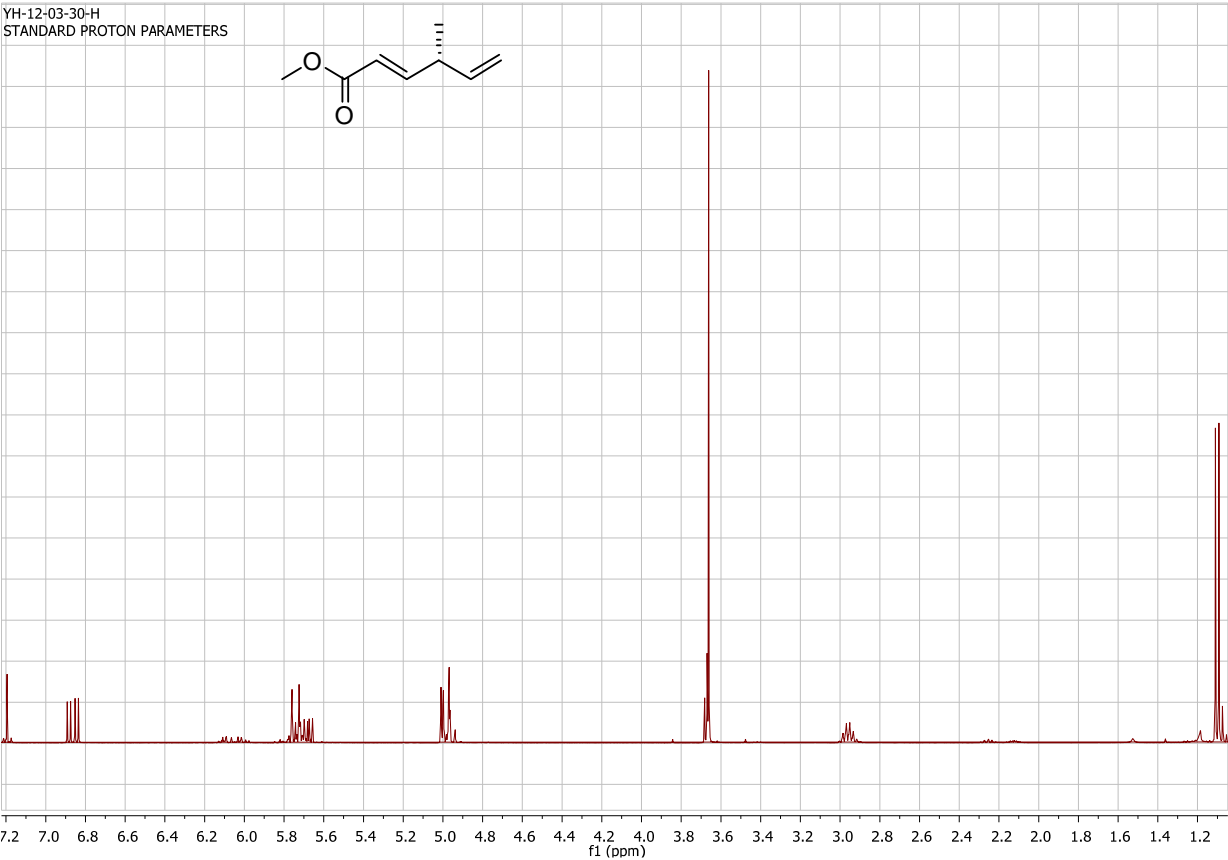




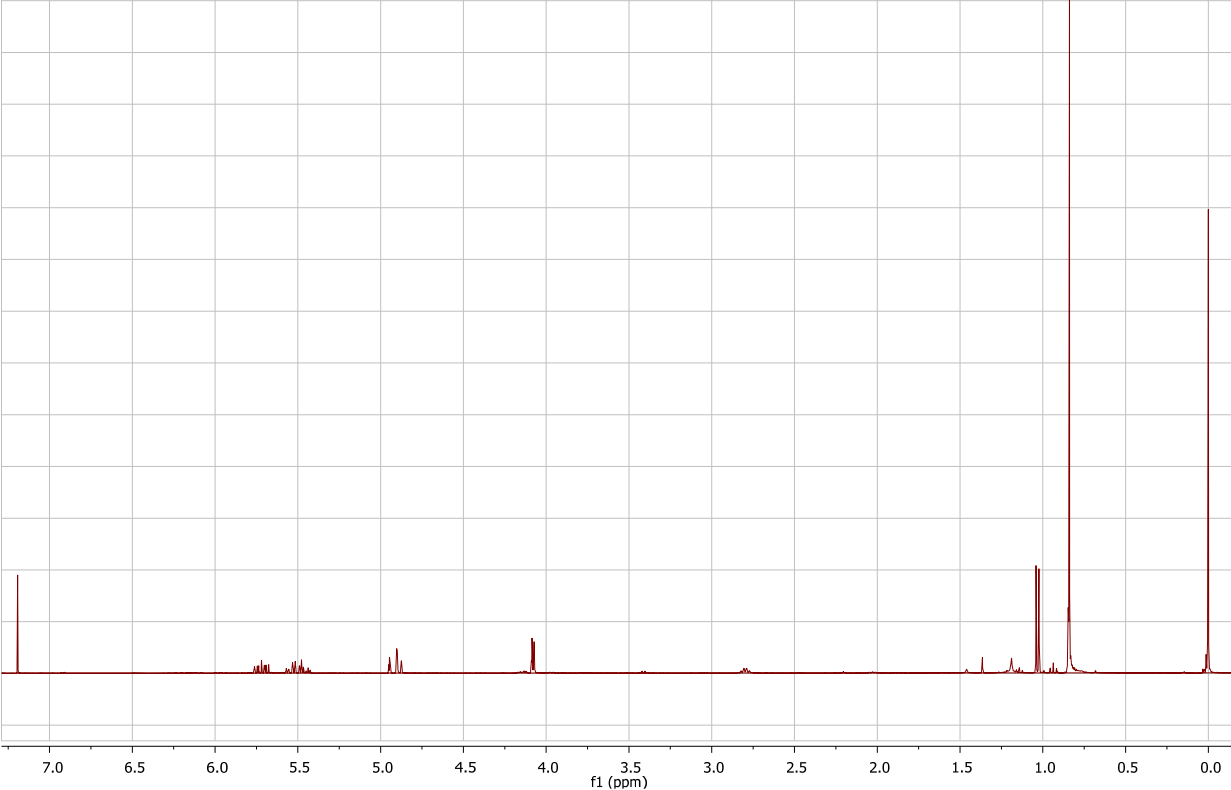
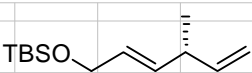




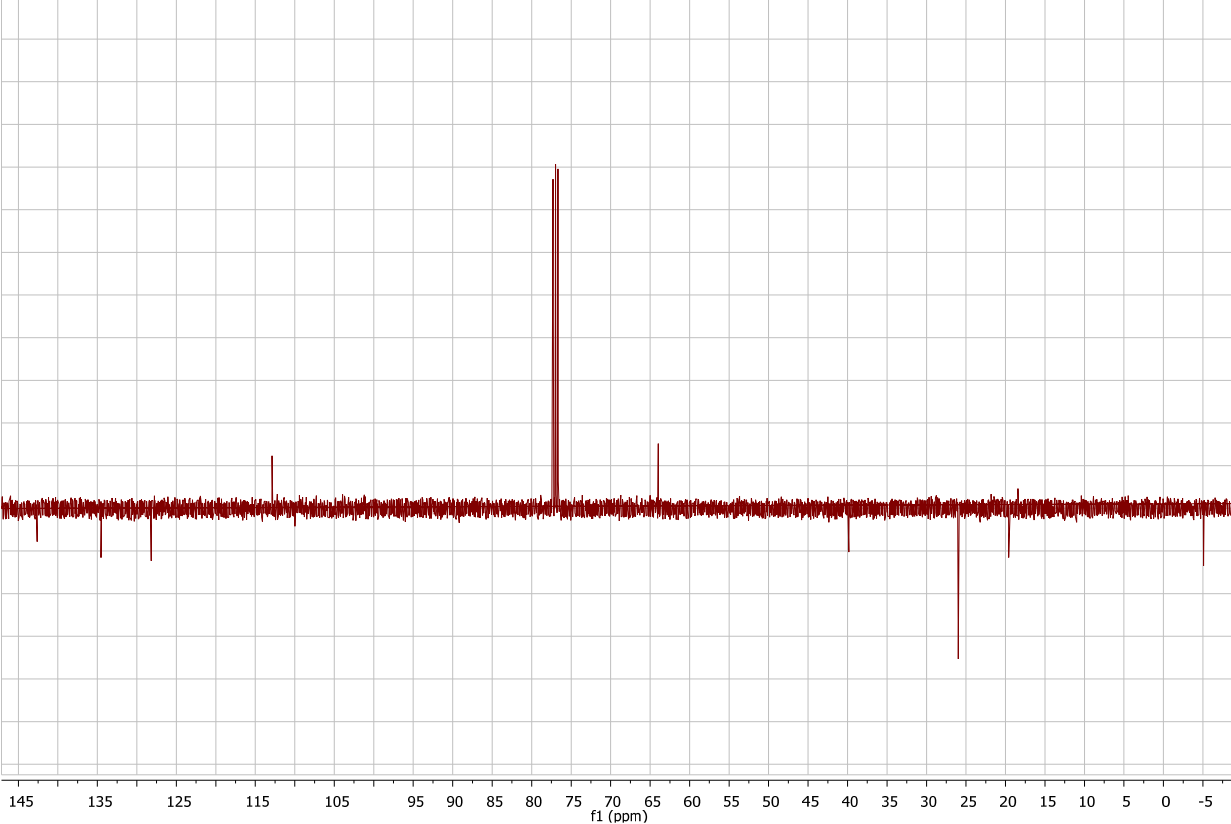


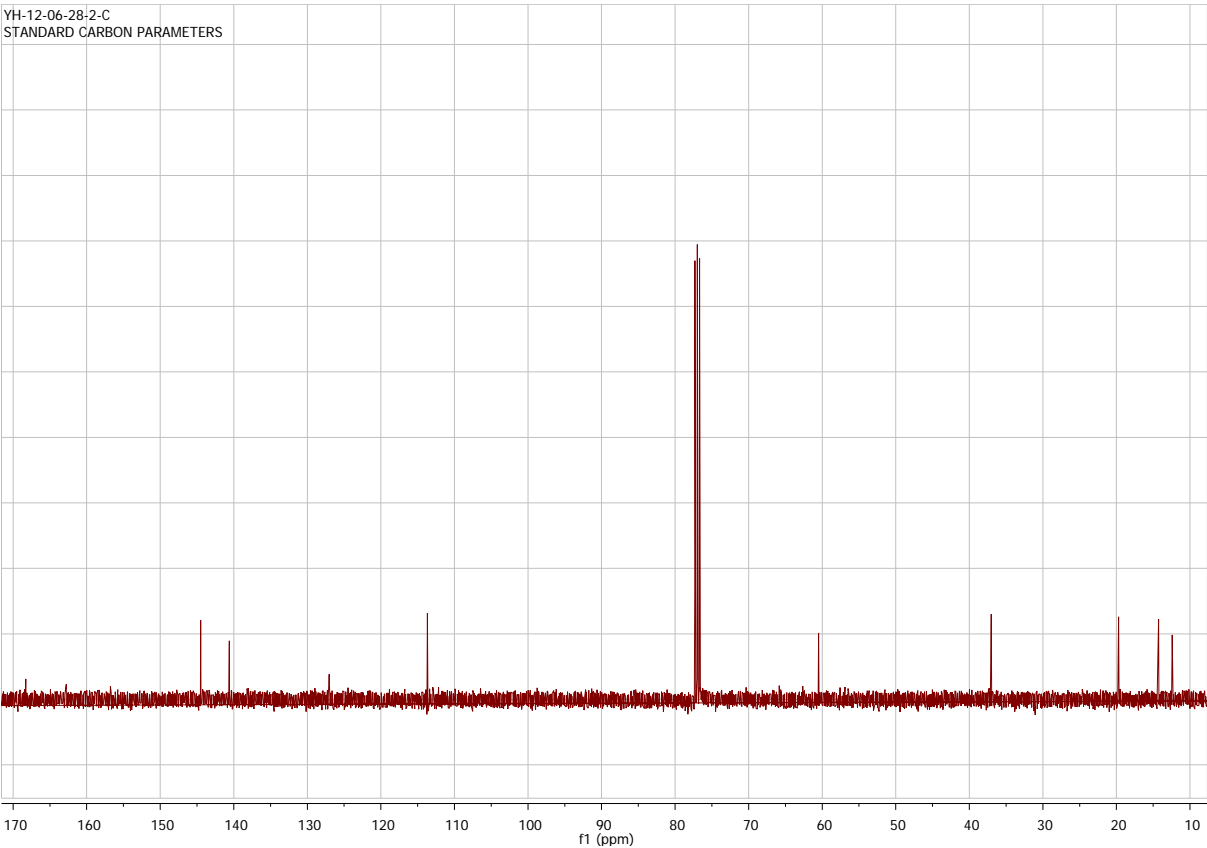
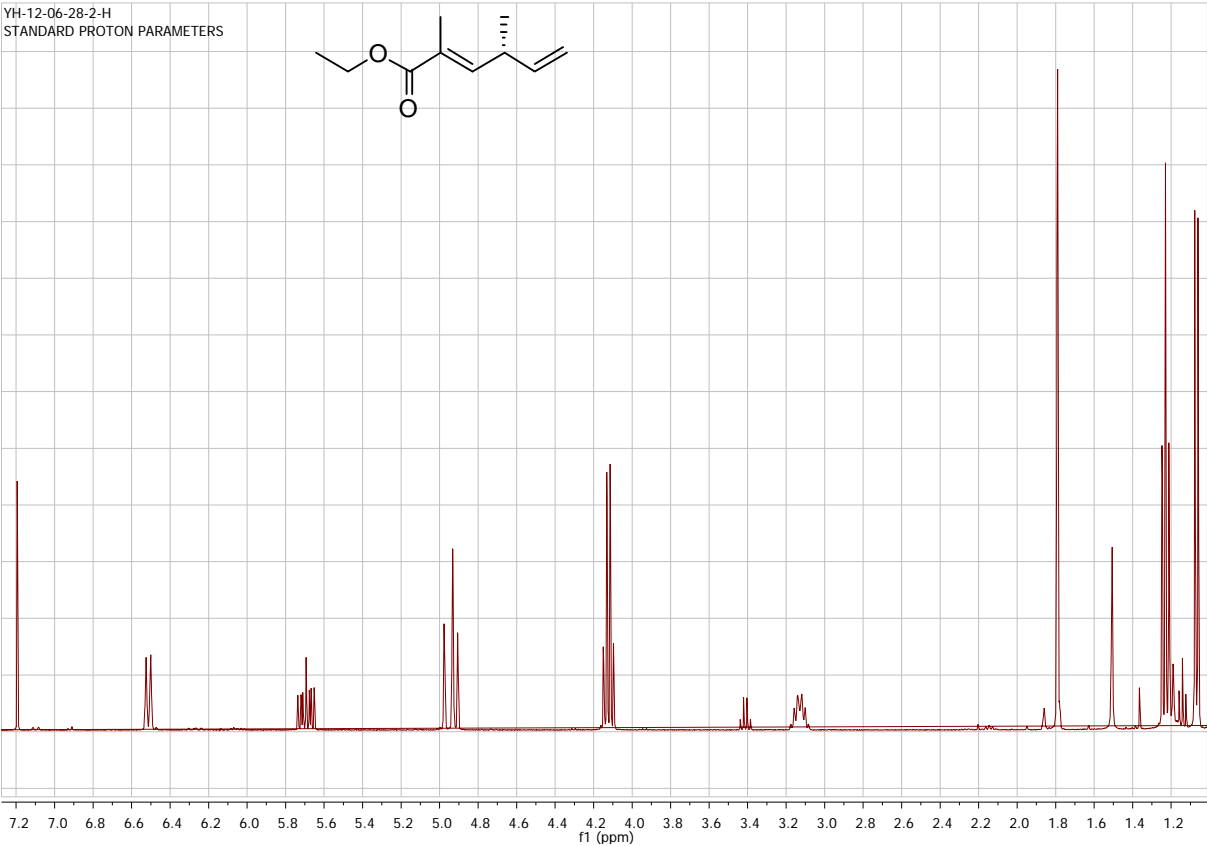


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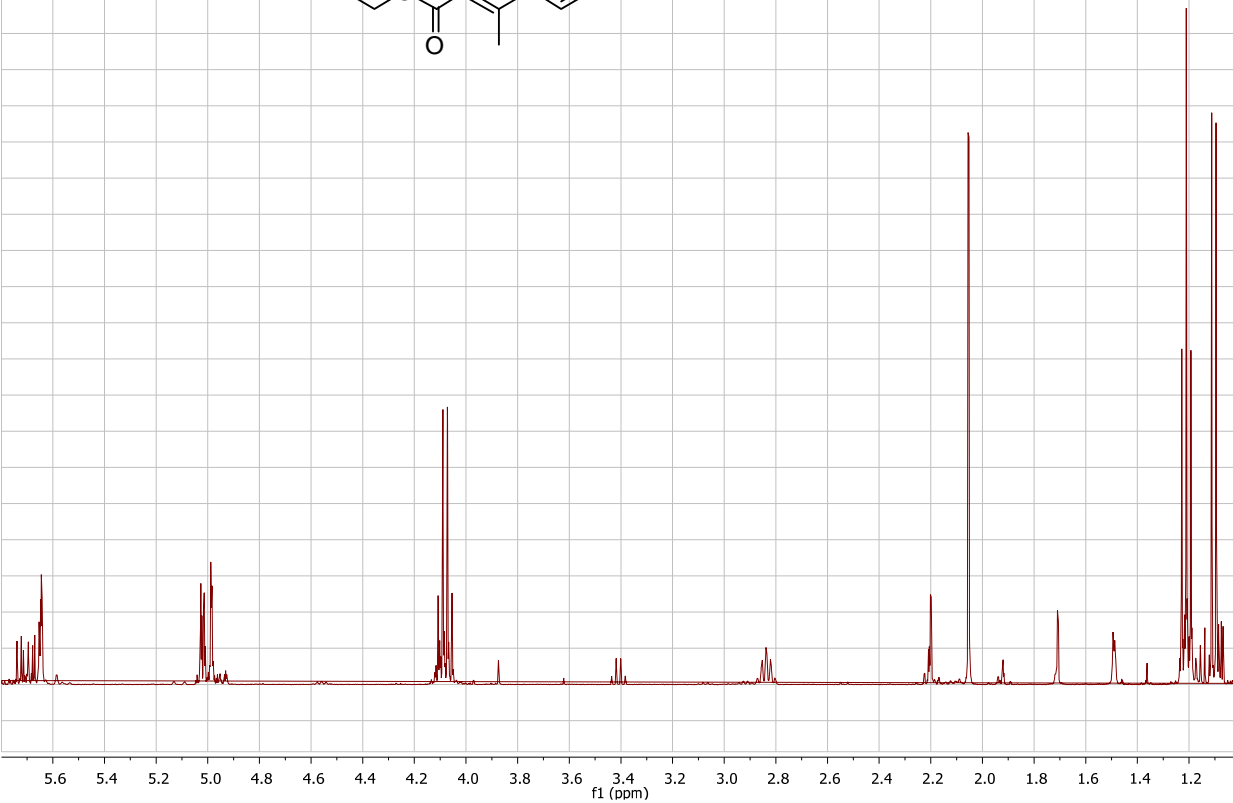
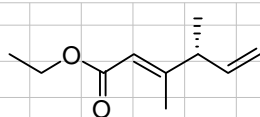


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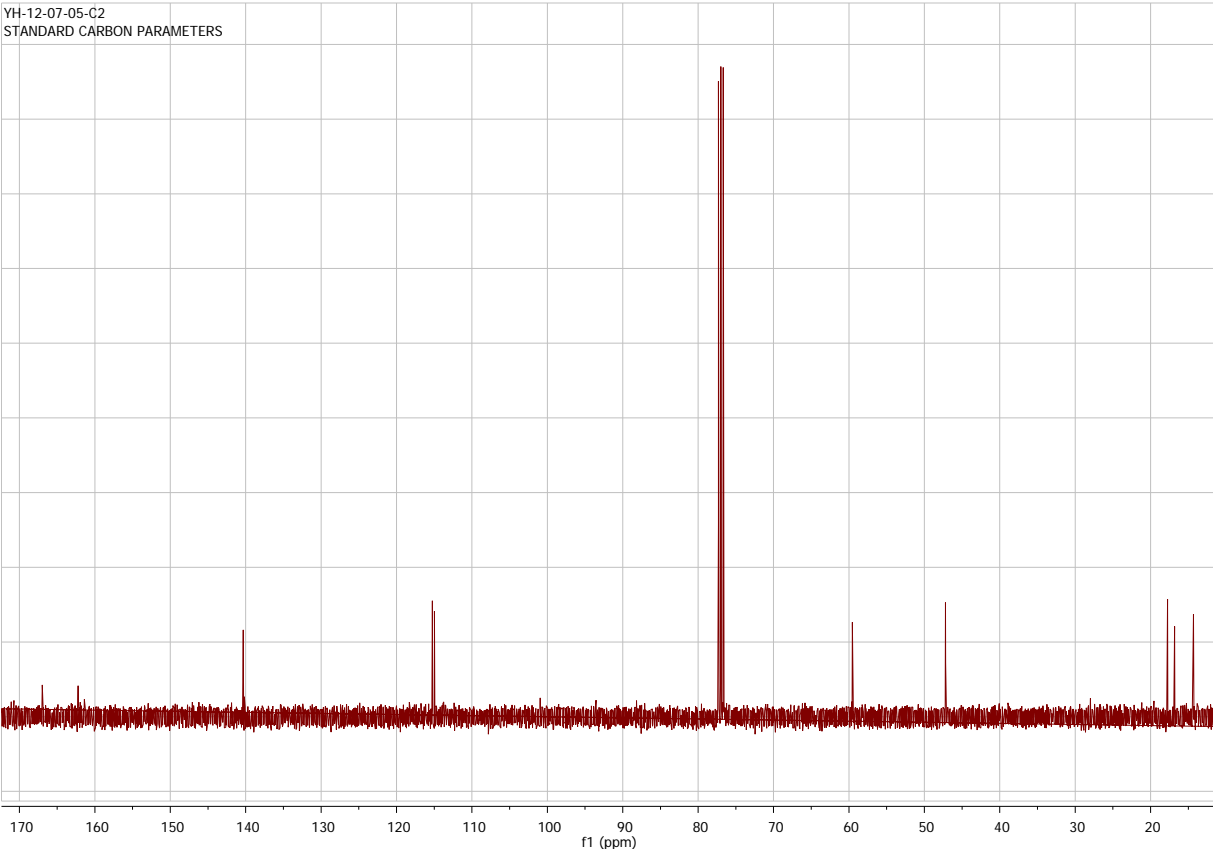




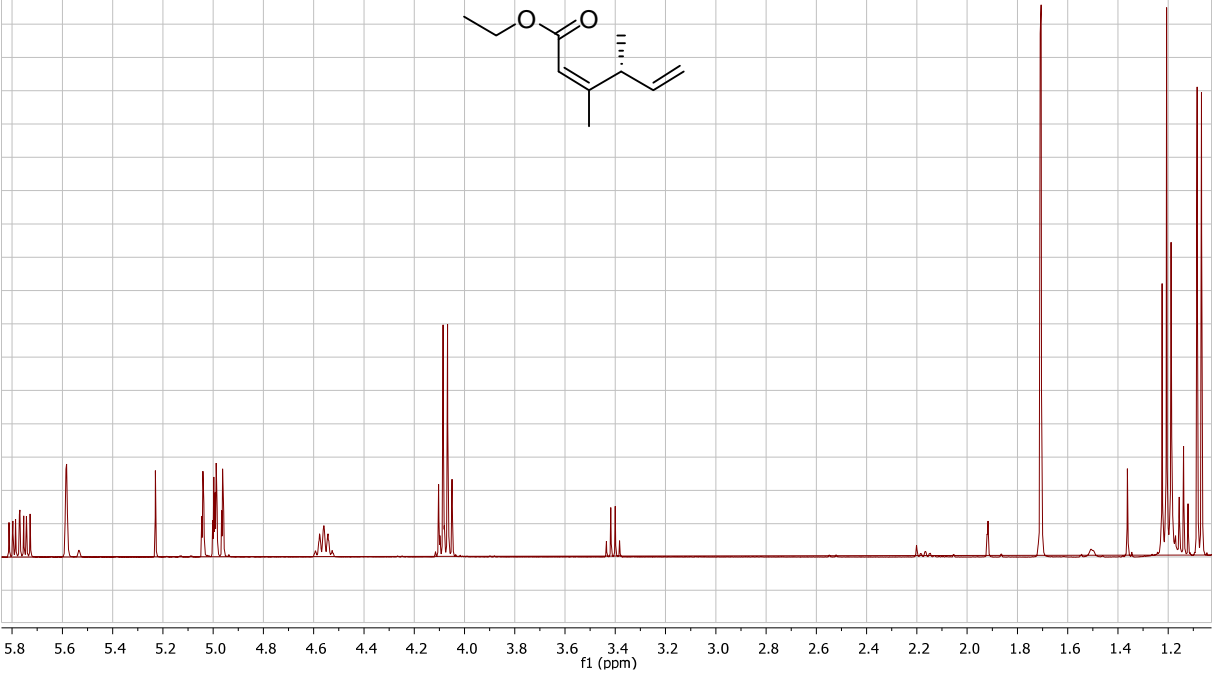
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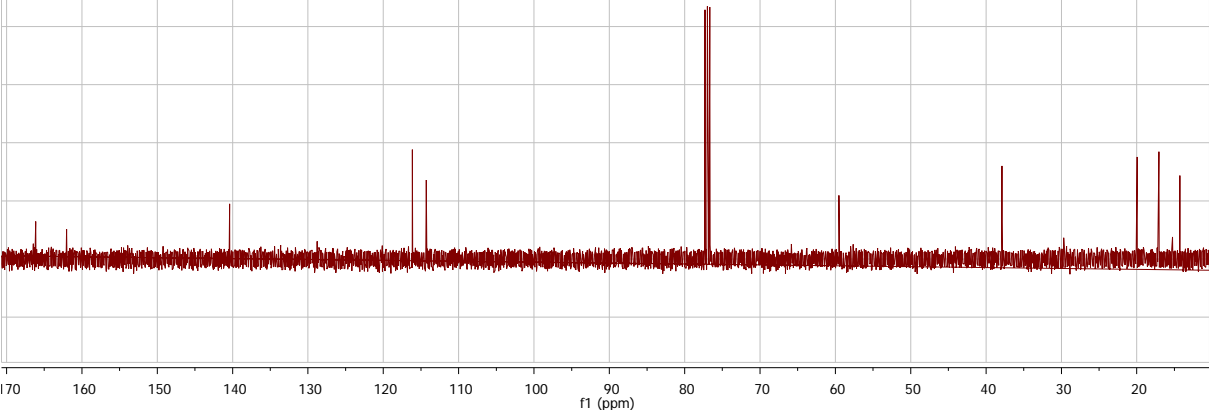
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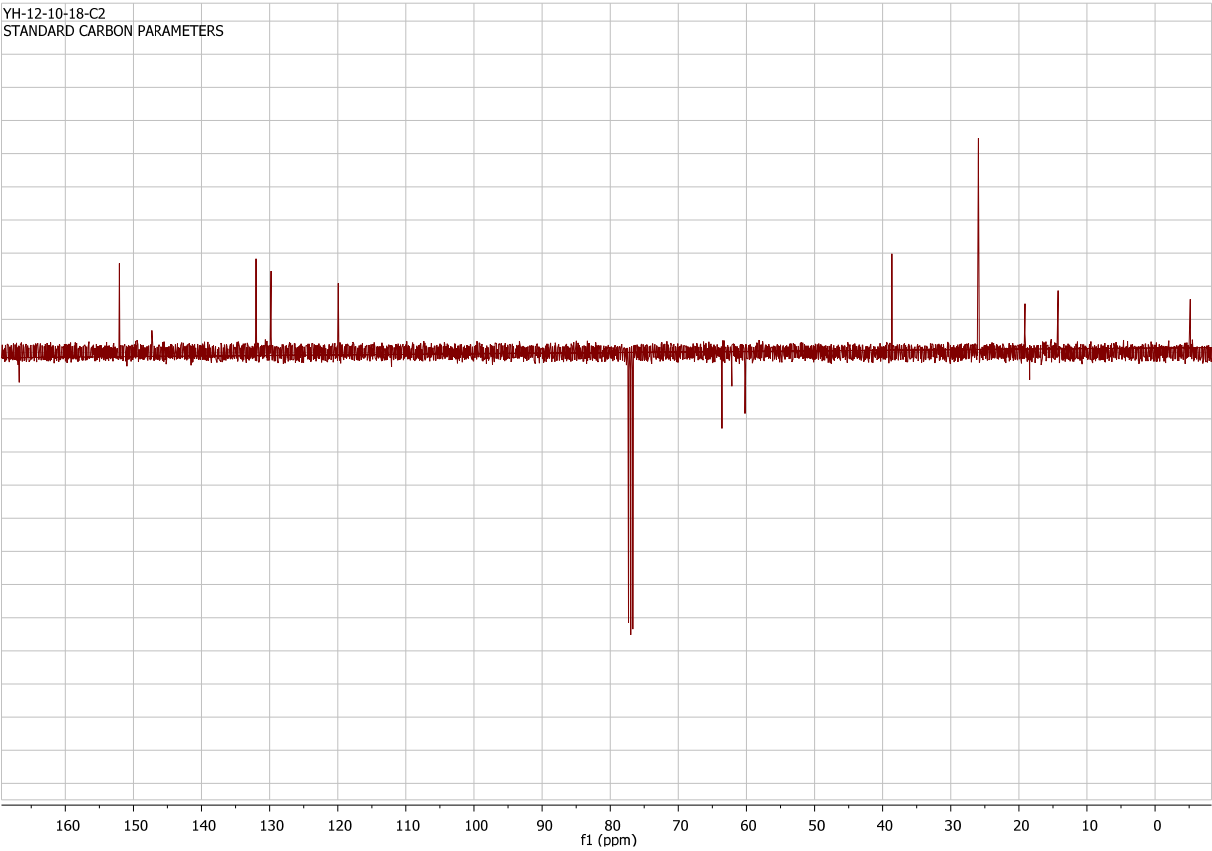
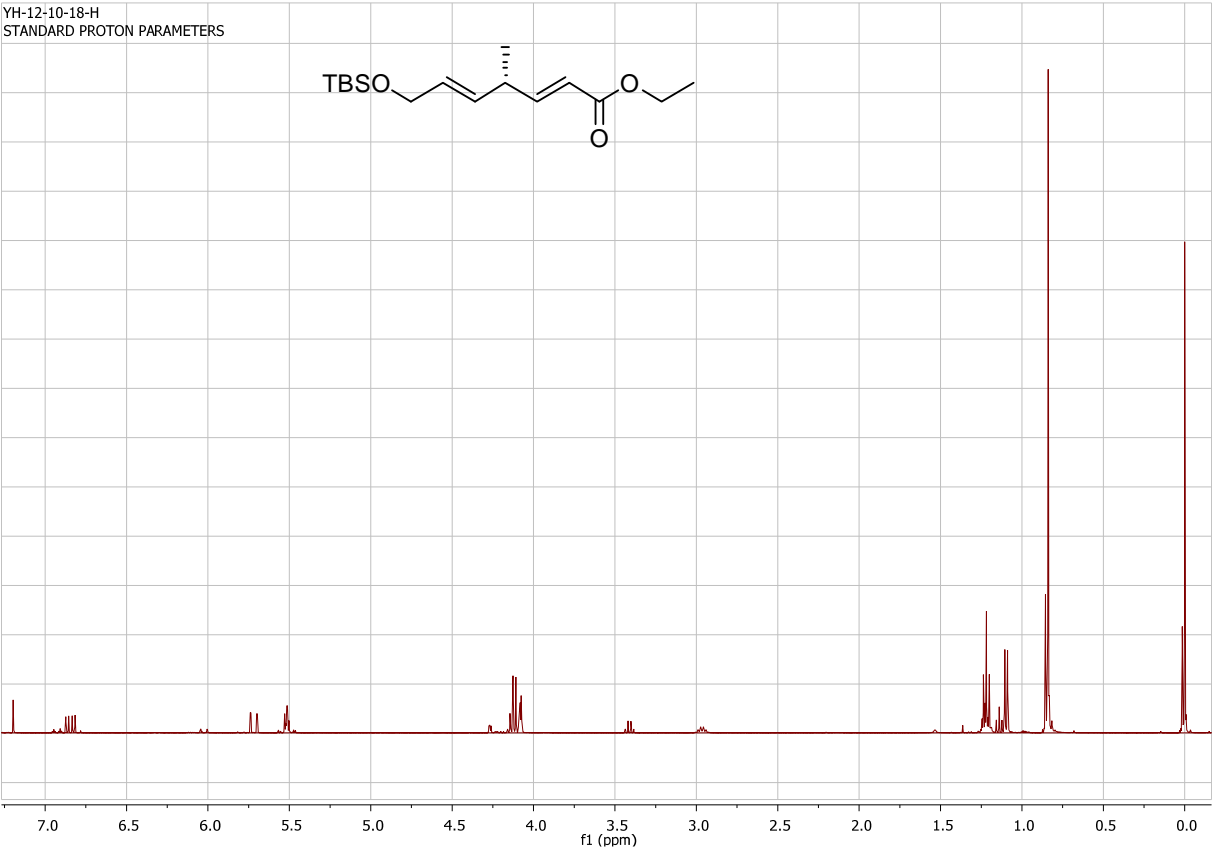


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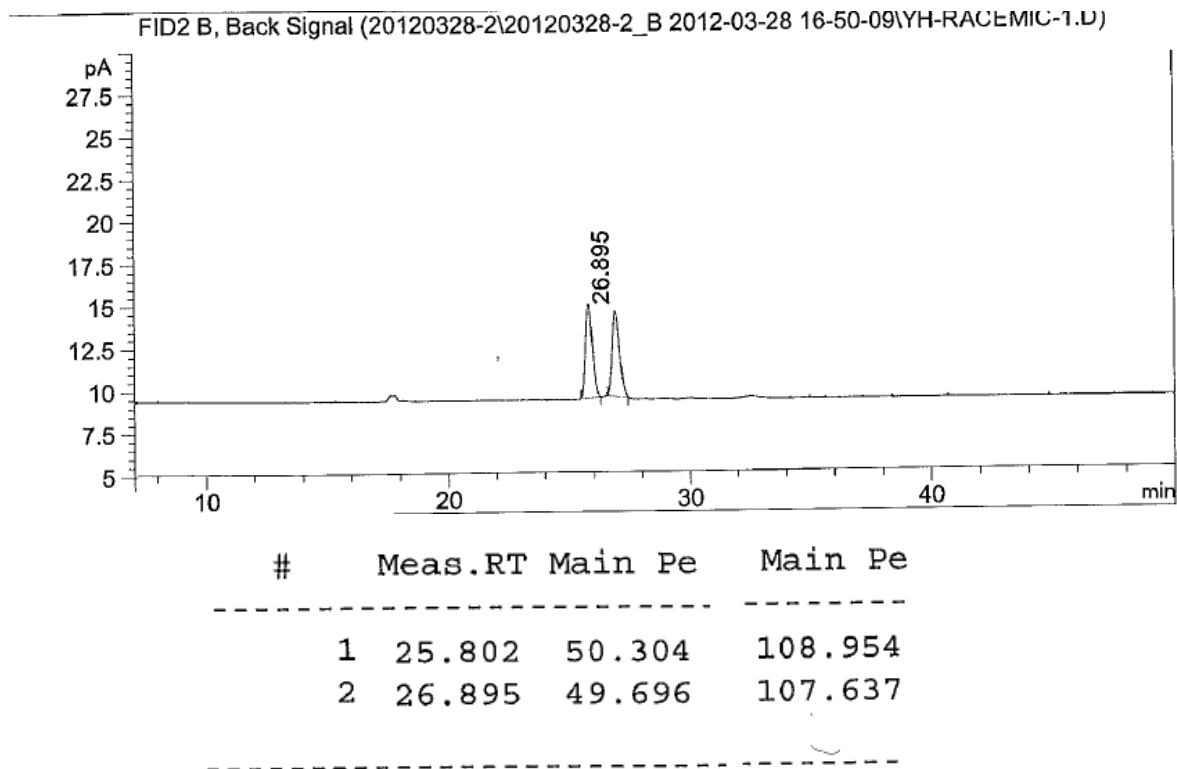


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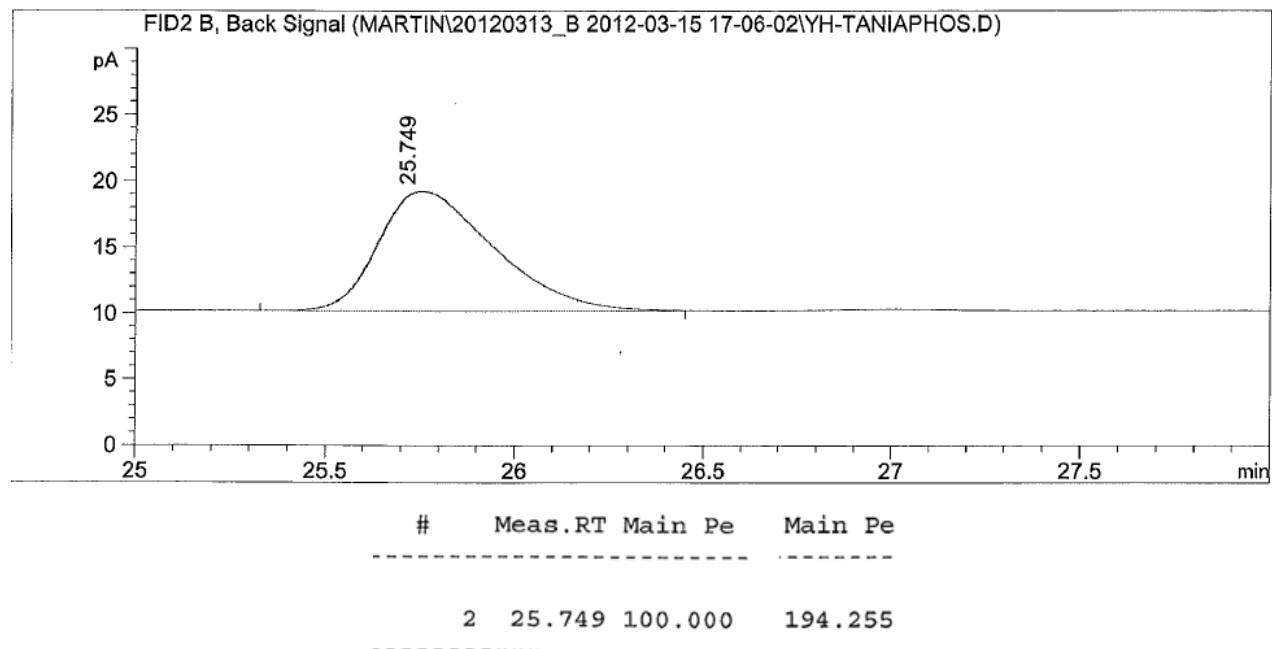




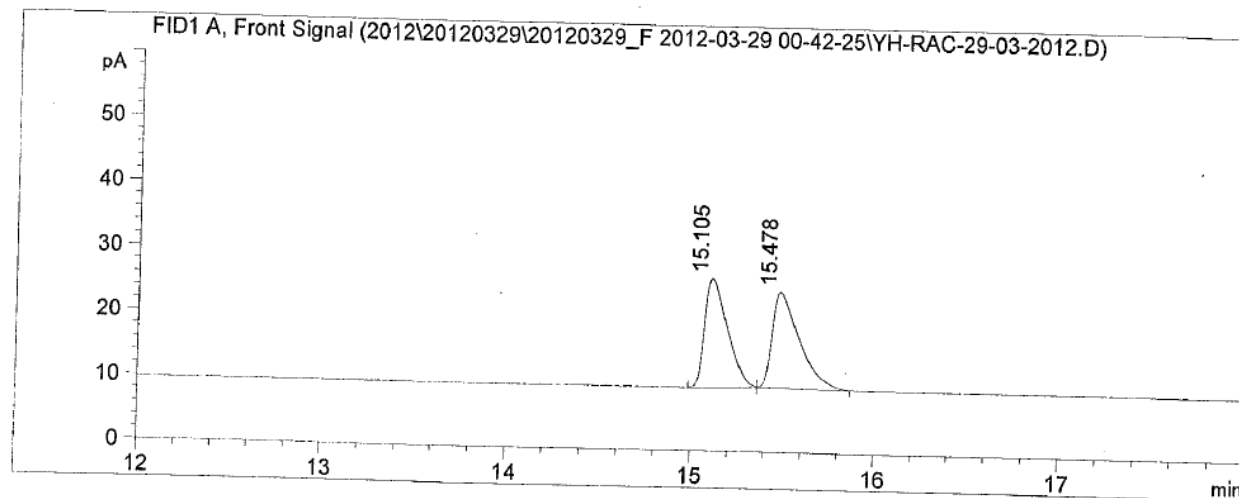
Racemic **2a**:



Optically active **2a**:

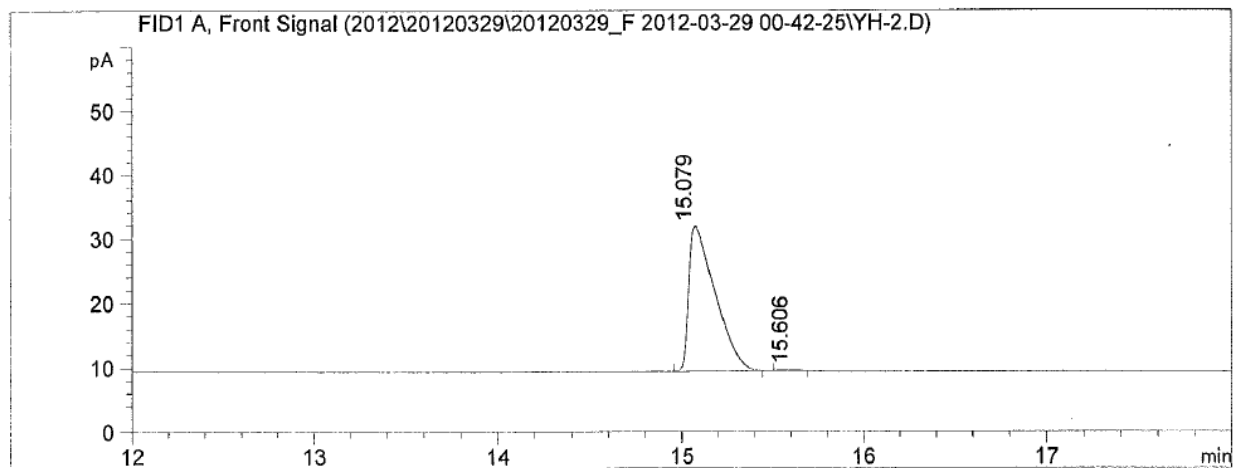


Racemic **2b**:



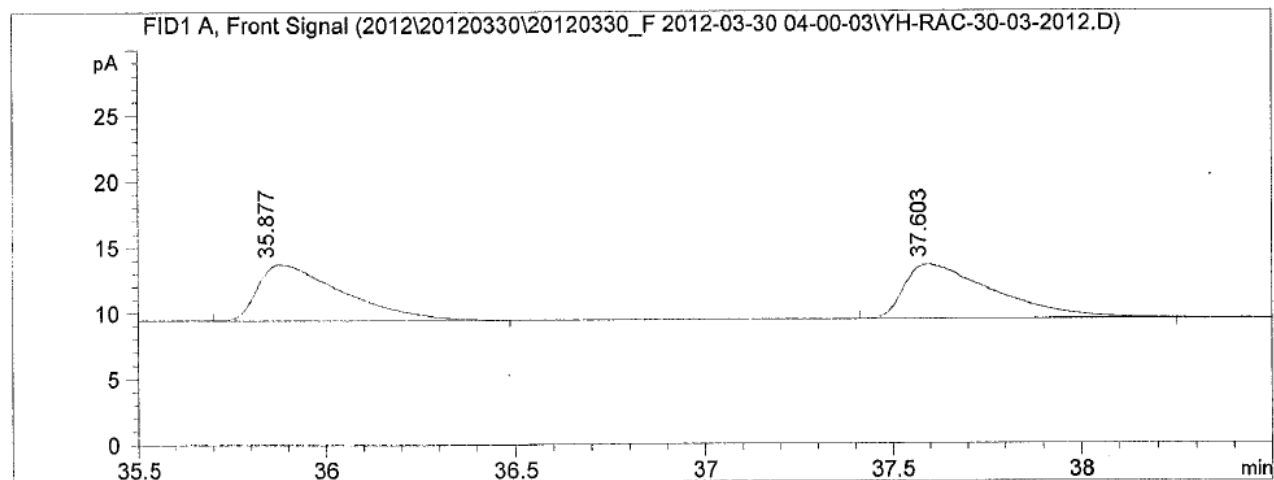
Main	Pe	Main	Pe	Meas.	RT
48.601	144.036	15.105			
51.399	152.330	15.478			

Optically active **2b**:



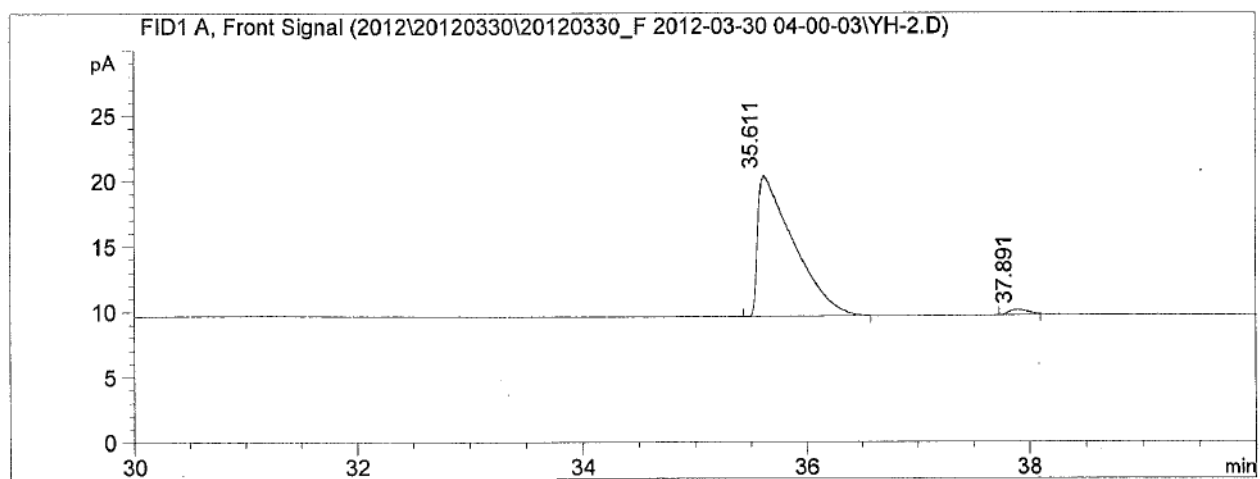
Main	Pe	Main	Pe	Meas.	RT
99.434	224.444	15.079			
0.566	1.278	15.606			

Racemic **2c**:



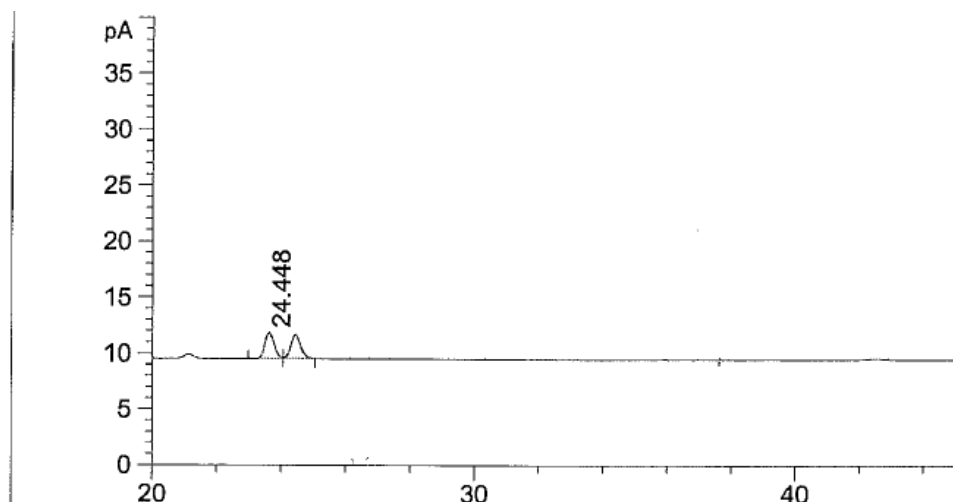
Main	Pe	Main	Pe	Meas.	RT
50.012	66.953	35.877			
49.988	66.922	37.603			

Optically active **2c**:



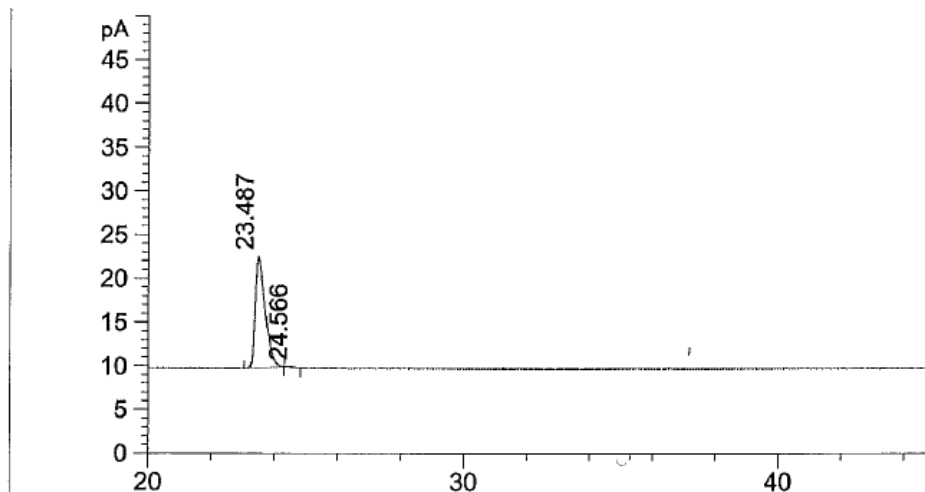
Main	Pe	Main	Pe	Meas.	RT
98.262	238.634	35.611			
1.738	4.220	37.891			

Racemic **2d**:



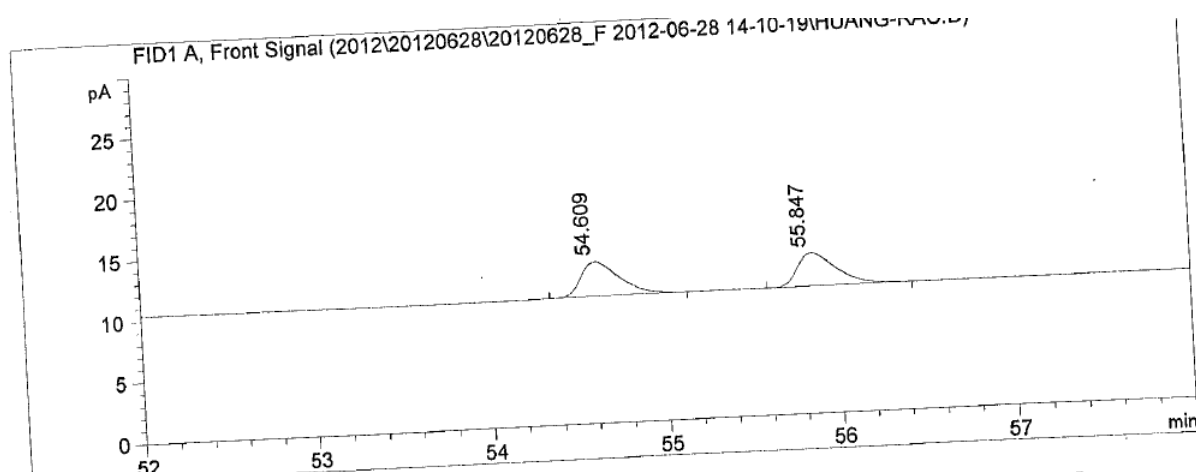
#	Meas.RT	Main Pe	Main Pe
1	23.631	50.167	44.902
2	24.448	49.833	44.603

Optically active **2d**:



#	Meas.RT	Main Pe	Main Pe
1	23.587	99.319	161.959
2	24.434	0.681	1.111

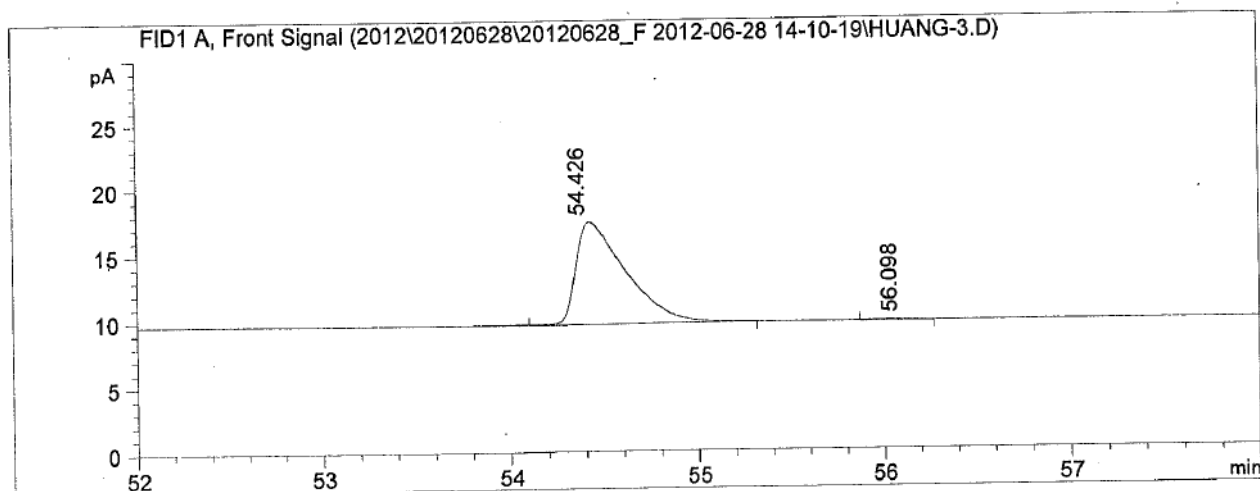
Racemic **2e**:



Main Pe Main Pe Meas.RT

50.519	42.732	54.609
49.481	41.854	55.847

Optically active **2e**:

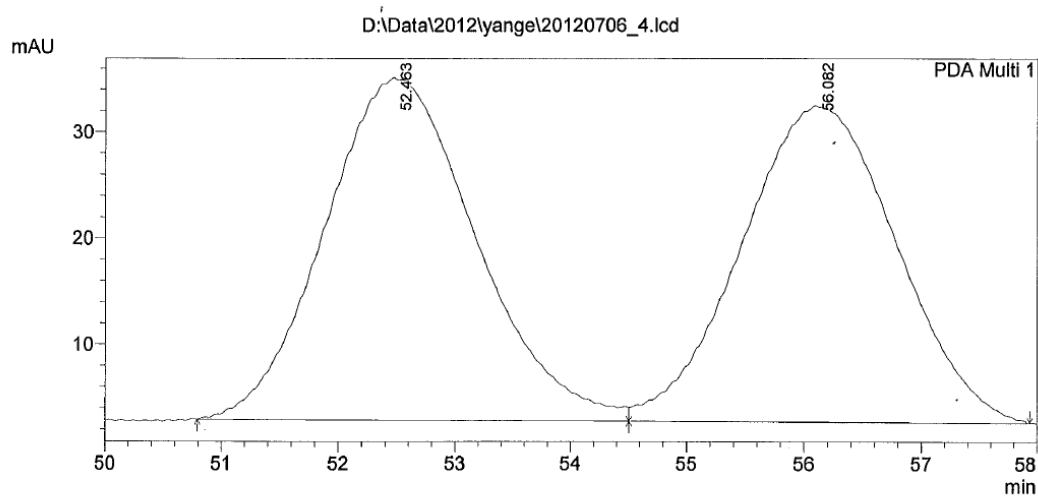


Main Pe Main Pe Meas.RT

98.768	141.958	54.426
1.232	1.771	56.098

Racemic **2f**:

<Chromatogram>



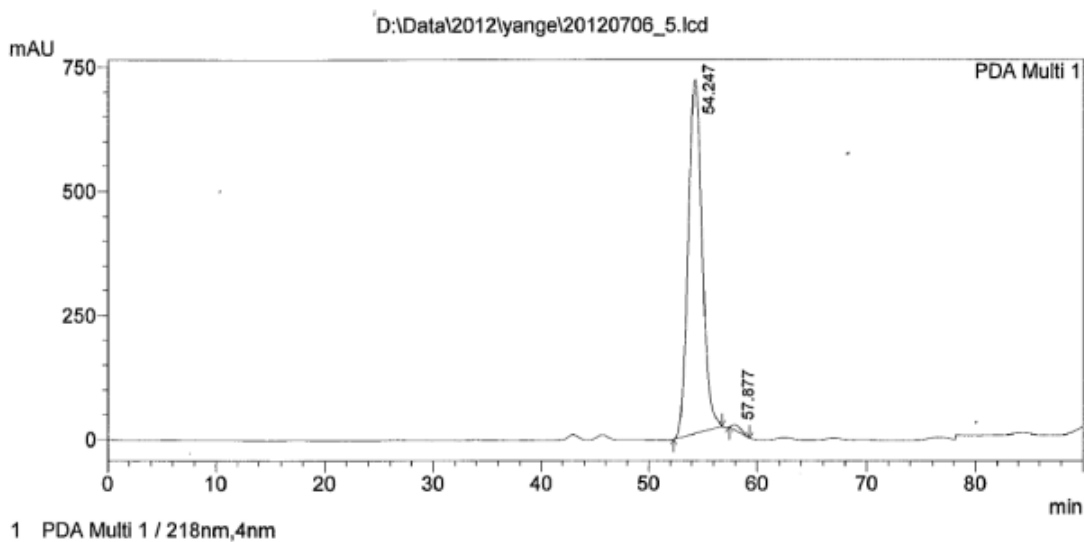
PDA Ch1 218nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	52.463	2905953	32265	51.614	52.002
2	56.082	2724247	29782	48.386	47.998
Total		5630200	62047	100.000	100.000

PeakTable

Optically active **2f**:

<Chromatogram>

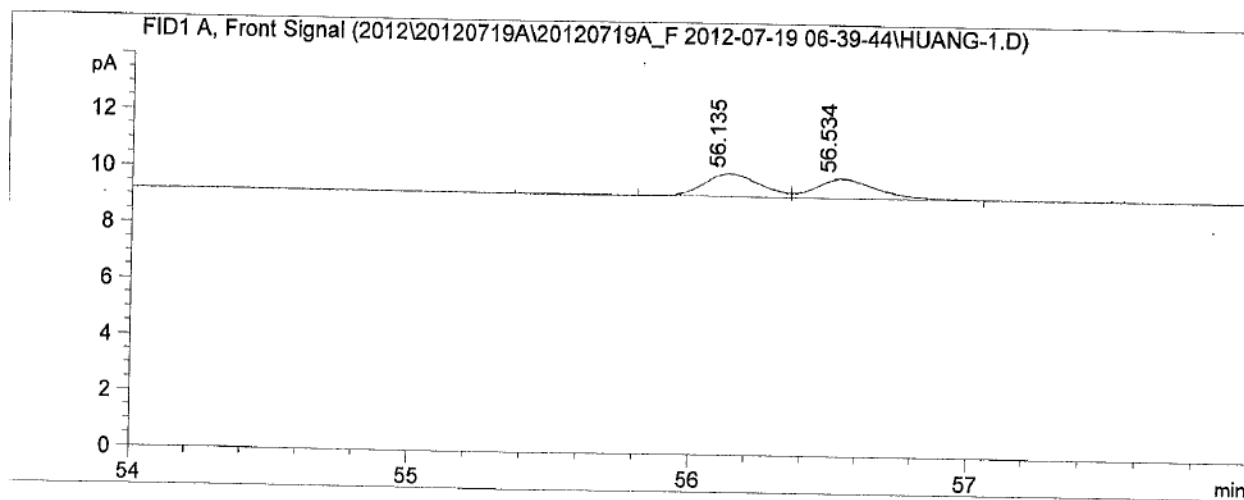


PDA Ch1 218nm

Peak#	Ret. Time	Area	Height	Area %	Height %
1	54.247	63652700	712033	98.969	98.596
2	57.877	663420	10142	1.031	1.404
Total		64316119	722175	100.000	100.000

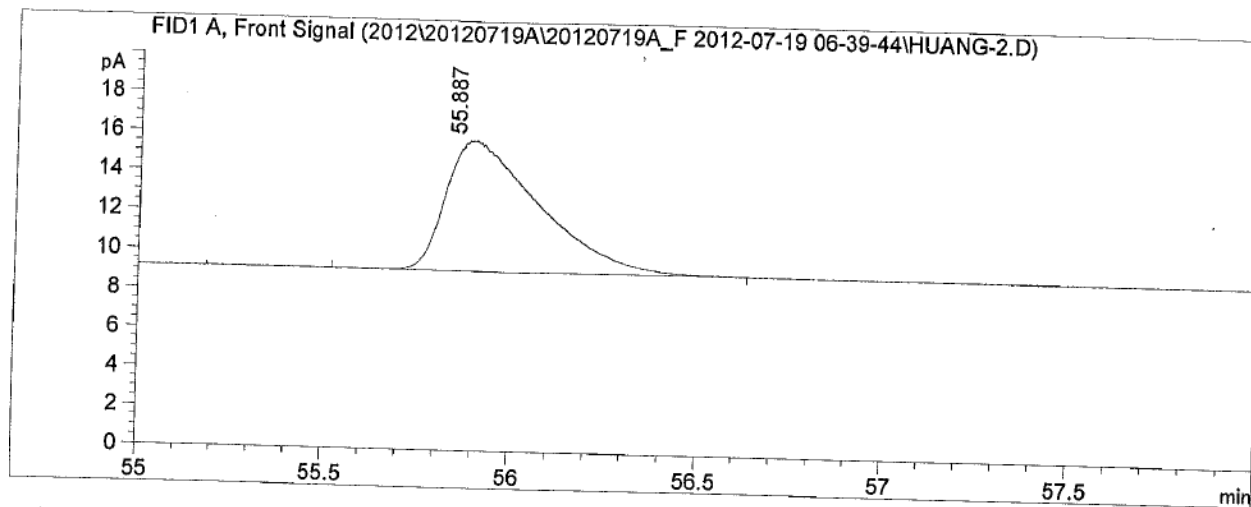
PeakTable

Racemic **2g**:



Main	Pe	Main	Pe	Meas.	RT
50.647	11.023	56.135			
49.353	10.741	56.534			

Optically active **2g**:



Main	Pe	Main	Pe	Meas.	RT
100.000	114.034	55.887			